CELLULOSE
CHEMISTRY

By

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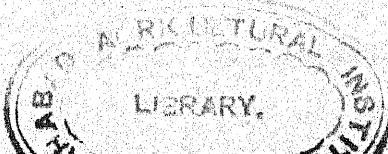
FOREWORD

THE importance of cellulose, as the essential organic raw material in textiles, and in the manufacture of paper, rayon, cellophane, explosives, lacquers, photographic films, and in plastics generally, is too well known to require discussion. Several important monographs dealing with the chemistry of this substance are now in press. These will cover the subject in the greatest detail and will serve as standard works of reference.

Dr. Plunguian's book however serves a different, less ambitious, but none the less useful purpose. It is written largely for the chemist beginning in this field or working in allied fields. It intends to give him a brief insight into cellulose chemistry and finds its best expression in the final chapter in which the recent work in this field is evaluated. This book will be welcomed by the busy reader keen to orientate himself in an important, interesting and rapidly developing branch of chemistry.

<div align="right">LOUIS E. WISE</div>

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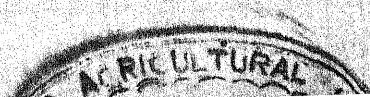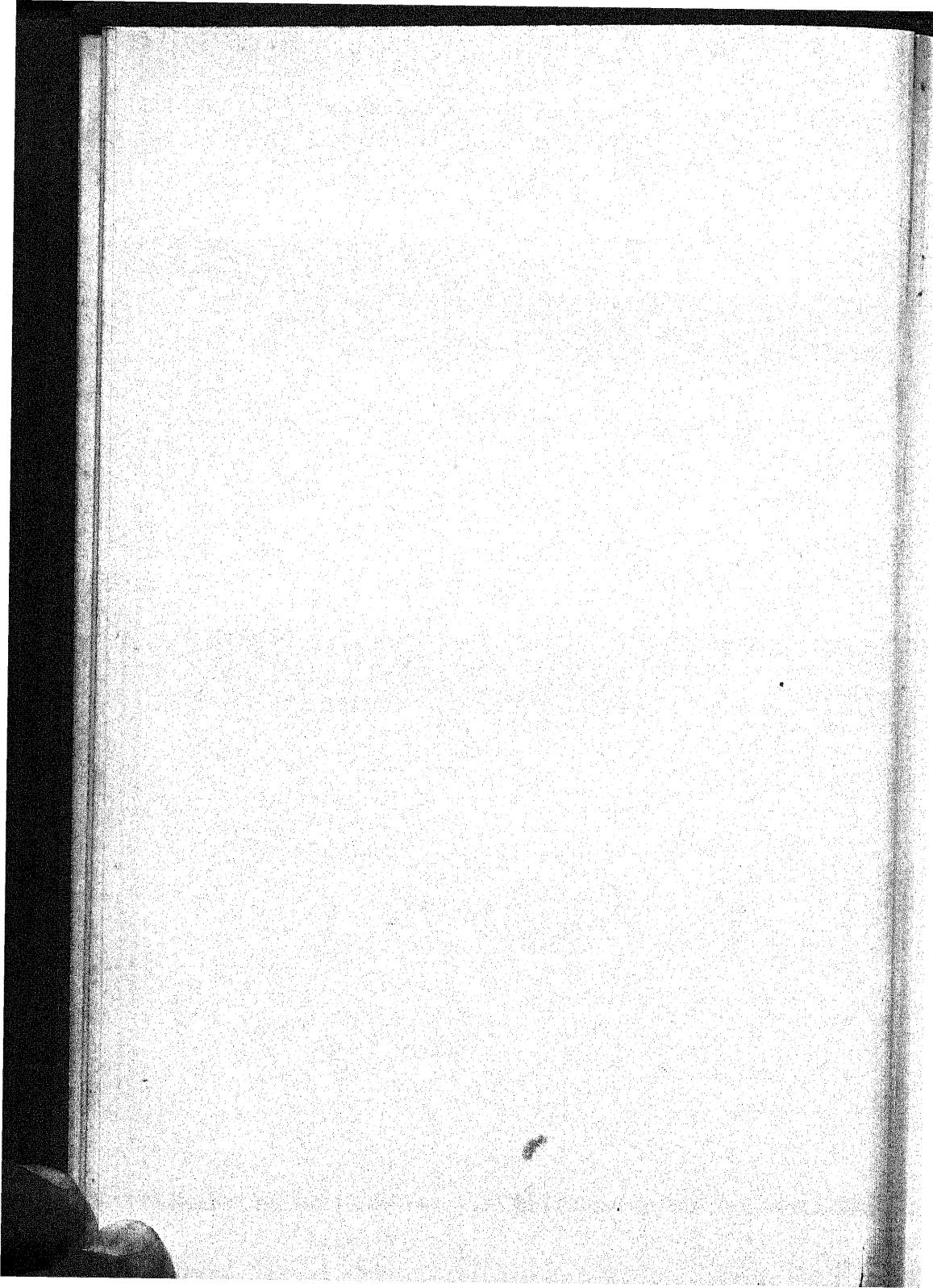
PREFACE

THIS book was designed primarily as a brief and up-to-date introduction to the chemistry of cellulose for non-cellulose chemists. An effort has been made to achieve a comprehensive outline of modern cellulose chemistry through a concentration of pertinent detail. It is hoped that this book will also serve the practising cellulose chemist who may wish to review the latest developments in this field. Interpretation of reactions, wherever possible, was made on the basis of the modern conceptions of the micellar structure of cellulose. This is taken up fully in the last chapter in the course of the logical development of the subject; some readers may find it advisable to consult this chapter earlier.

The author is greatly indebted to Professor Edwin C. Jahn of the New York State College of Forestry for constructive criticism and helpful suggestions.

The author is grateful to Dr. Milton Harris, Dr. William M. Harlow, and Dr. Harry F. Lewis for the photographs and cuts. Acknowledgment is made to the Williams and Wilkins Company for permis-

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The author has been fortunate in having the able assistance of his wife, Mrs. Gina Plunguian, in the preparation of the manuscript and to her much credit is due for her care and generous cooperation. The author is also under obligation to Mr. Basil Outerbridge of the Homasote Company for valuable assistance.

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CELLULOSE AND ASSOCIATED SUBSTANCES

CELLULOSE forms the major portion of the cell walls of the higher plants and is the basic constituent of all plant life. Cellulose far outranks all other natural organic substances in abundance and diversity of sources. It has been estimated that all carbon compounds occurring in plant vegetation correspond to 1,098,000,000,000 kilograms of carbon dioxide.[33] Over 90% of this occurs in trees; the major constituent of the tree is cellulose.

There is considerable variation in the cellulose content of various plant tissues. The dry substance of young leaves may have less than 10% cellulose. In older leaves it may reach 20%. Straw contains about 35% cellulose. The woody tissues of trees and shrubs contain approximately 60% cellulose. Flax fiber contains about 80%, while the seed hair of the cotton plant may consist of over 90% cellulose. This is the highest known cellulose content of any naturally occurring substance.

Beginnings of Cellulose Chemistry

The chemistry of cellulose had its beginning more than 100 years ago. In 1838 Payen succeeded for the first time in separating various plant tissues into their components. He recognized cellulose as the main constituent of the cell wall and expressed the view that the other non-cellulose constituents were not combined chemically, but existed in intimate mechanical mixture, determined by the conditions of growth.

Payen thought at first that all components of the cell wall with the composition $C_6H_{10}O_5$ were identical with cellulose. It remained for E. Schulze in 1891 to establish the existence of different "celluloses." On hydrolyzing cell wall carbohydrates with dilute acids only cellulose remained unaffected. He found that this more resistant component would yield glucose on further hydrolysis with strong acids, while the easily hydrolyzed components yielded other sugars. Schulze therefore proposed the term "hemicelluloses" for the less resistant polysaccharides. This term has been retained to this day, although it is now known that these hemicelluloses are not derivatives of cellulose, but are other polysaccharides.

The cell wall component which Payen called "incrusting substance" was termed "lignin" by F. Schulze in 1857. It now refers to the non-carbo-

hydrate component of the plant cell wall, obtained either by difference after removing the carbohydrate fractions by acid hydrolysis, or obtained directly by solution in alkaline or certain organic solvents.

Payen was emphatic in claiming that the cell wall components existed merely in mechanical distribution. He visualized the process of lignification as a gradual infiltration of incrusting material into the cellulose tissue. Later, in 1866, Erdmann suggested that the cellulose and non-cellulose components could be combined chemically, as in the form of an ester. This led to the strange conception of wood substance being composed of a complex but uniform single compound. Even as late as 1920, the great English cellulose chemists Cross and Bevan [6] still spoke of various "compound" celluloses, such as lignocellulose and pectocellulose, as definite compounds to which they assigned empirical formulas.

This view had its origin in the difficulty of separating cellulose from the other cell wall components. Drastic hydrolyzing conditions are required to remove the "encrusting materials," lignin and hemicellulose. The view of "compound" celluloses is no longer tenable because the known structure of the cellulose micelle or crystallite leaves no room for these other components. However, cell wall lignin and cellulosans may interpenetrate into the amorphous regions of the cellulose tissue, thus

effectively blocking the action of dispersing media. "Cellulosans," according to Norman,[28] include those hemicelluloses which are part of the cellulosic framework substance or cell wall.

The term micelle is derived from the "micellar theory" proposed by Naegeli in 1858. According to this theory, organized organic tissue is not built up directly from the molecules but from submicroscopic groups of molecules which he called micelles. This term is still employed. However, it no longer means an individual structural element, but a region where the tendency toward crystallization predominates. The structure surrounding these regions consists of amorphous fringes of chain molecules which are less well organized. As now used, "micelle" is synonymous with "crystallite" meaning a submicroscopic crystalline unit built up of molecules of unequal length. (The term "crystal" refers to a crystalline unit which is microscopic or larger and is built up of molecules of equal size.)

Brief Review of the Chemistry of Cellulose

Cellulose belongs to the carbohydrate family of compounds. It is composed of carbon, hydrogen and oxygen with the hydrogen and oxygen present in the same ratio as in water; it contains 44.4% carbon, 6.2% hydrogen, and 49.4% oxygen for which the simplest empirical formula is $C_6H_{10}O_5$. Since cellulose is a colloidal substance, its formula evi-

dently is $(C_6H_{10}O_5)_n$, i.e., it has a high molecular weight. It can be hydrolyzed almost quantitatively to glucose, $C_6H_{12}O_6$, showing that cellulose is made up of anhydroglucose units. Esterification and etherification reactions yield trisubstituted derivatives showing that each unit contains three free hydroxyl groups. On methylation a trimethyl cellulose is formed which on hydrolysis yields only 2, 3, 6-trimethyl glucose, hence, the hydroxyl groups are located on these carbon atoms. The hydroxyl groups on the 2 and 3 carbon atoms are secondary alcohols while that on the 6 carbon atom is a primary alcohol.

Cellobiose octaacetate is obtained from cellulose by a combination of acetylation and hydrolysis known as acetolysis, indicating that the anhydroglucose units are united by cellobiose linkages. This linkage is a glucosidic oxygen bond between carbon atoms 1 and 4 of adjacent units. The structural anhydroglucose units are six-membered amylene oxide rings in which carbon atoms 1 and 5 are joined by an oxygen bridge.

Cellulose from all sources has the same chemical composition. However, there may be considerable variation in the length of molecular chains and in the degree of orientation in the structural cellulose tissue.

The terms alpha, beta and gamma cellulose relate to the fractionation of cellulose by treatment with 17.5% sodium hydroxide solution at room tempera-

ture. Alpha-cellulose is the fraction which remains undissolved, beta-cellulose dissolves but may be precipitated by acidification of the alkaline solution, while gamma-cellulose remains in solution. These differences are due to variations in the length of molecular chain as well as the inclusion of hemicelluloses such as xylan. Cotton has a high alpha-cellulose content, about 98%, while wood pulp usually has a much lower content of alpha-cellulose and a correspondingly higher beta- and gamma-cellulose. Wood pulp may be used for the production of rayon and explosives in place of the usually preferred cotton linters. When such pulp is used for these purposes it must be subjected to a preliminary purification treatment with alkali and bleaching chemicals whereby the beta- and gamma-cellulose fractions are mostly removed.

The Hemicelluloses

The hemicelluloses are by definition those constituents of the plant cell wall which may be extracted by dilute alkalies. They may be hydrolyzed by hot dilute acids to give hexoses and pentoses. The type of simple sugar obtained depends upon the polysaccharide precursors, such as galactan, xylan, etc. Uronic acids, such as glucuronic and galacturonic acids are also obtained, for the hemicelluloses include polyuronides.

The sugars commonly found in plant hemicellu-

loses belong to two distinct configurational groups, i.e. (1) Glucose series: d-glucose, d-glucuronic acid and d-xylose and (2) Galactose series: d-galactose, d-galacturonic acid and l-arabinose. In the first group xylose frequently predominates and glucose may be present only in small amounts. In the second group galactose predominates.[28]

It is interesting to point out by means of structural formulas the exact configurational relationship that exists among the members of these two groups. From these it may be visualized how the hexose oxidizes to uronic acid which in turn yields the corresponding pentose by splitting off carbon dioxide.

d-GLUCOSE $+ O \longrightarrow$ d-GLUCURONIC ACID $- CO_2 \longrightarrow$ d-XYLOSE

d-GALACTOSE $+ O \longrightarrow$ d-GALACTURONIC ACID $- CO_2 \longrightarrow$ l-ARABINOSE
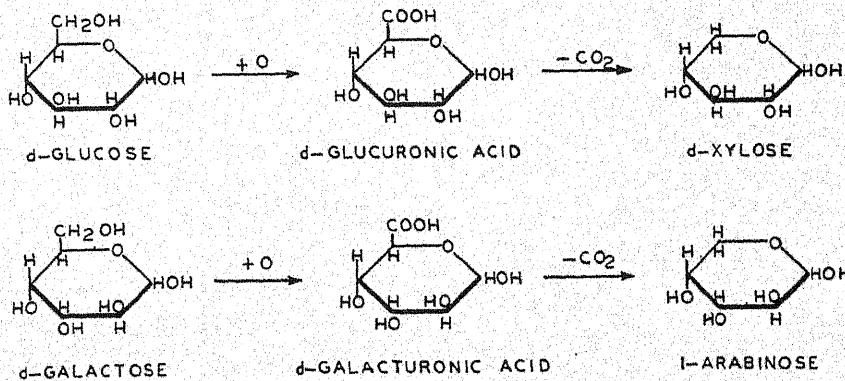
The hemicelluloses are divided into two distinct groups:[11] (1) The polyuronides which are not closely associated with cellulose and which contain considerable amounts of uronic acids. (2) Cellu-

losan (derived from a combination of the words cellulose and hexosan or pentosan) meaning those hemicelluloses intimately associated with cellulose and not containing uronic acid. The cellulosan found in most structural cellulose is the polysaccharide xylan, giving the pentose sugar d-xylose on hydrolysis.
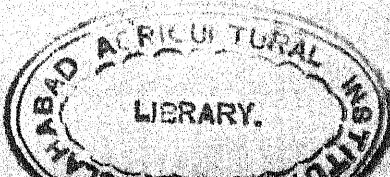
The hemicelluloses can be extracted from plant tissue only by means of 4–5% sodium hydroxide solution, while the isolated preparations and fractions may be readily soluble in water to give an opalescent solution. This has been variously interpreted as pointing to the existence of the hemicelluloses *in situ* in combination with another cell wall constituent, namely, lignin. The hemicelluloses are non-reducing and in spite of the presence of uronic acid groups do not exhibit apparent acidic properties. Some hemicelluloses are precipitated from alkaline solution by addition of acid and exhibit a critical pH value at which precipitation is most complete and flocculation most rapid. When dried from water, they form an extremely hard, horny mass which redissolves with great difficulty.

The hemicelluloses are characterized by the conversion of their pentose units to furfural when boiled with dilute acid. This method now forms the commercial source of furfural, the hemicelluloses being derived from waste oat hulls.

Holocellulose

Another combination of cell wall components which may be obtained by experimental manipulation is holocellulose. This is the fraction obtained from wood by alternate treatment with chlorine and alcohol-pyridine or with chlorine and 95% alcohol containing 3% monoethanolamine. These methods serve to delignify the wood without removing any of the carbohydrate portions. Holocellulose may therefore be considered as the sum total of the non-lignin substances of the cell wall.[38, 39]

Lignin

In contradistinction to the hemicelluloses, the lignin component of the cell wall is much more difficult to extract. It may be separated by the use of drastic reagents or with reagents which chemically combine with the lignin, forming a derivative. This serves to alter the character of the preparations in accordance with the method of separation employed.

The general methods of lignin separation may be divided into two groups: (1) Those methods which depend upon dissolving the cellulose and other carbohydrates and leaving the lignin as a residue and (2) those that dissolve the lignin and thus separate it from the other constituents.

An example of the first group is the Klason

method or the use of 72% sulphuric acid. The plant material is first extracted with alcohol-benzene to remove the resins and oils and then with hot water to remove other "extractives." It is then treated with 72% sulphuric acid at 20°C. for two hours. This acid concentration is reduced to 3% by diluting with water and the suspension is boiled for three hours before filtering, washing, and drying. Examples of the second group are those used in the technical process of pulping wood chips, which will be described later, namely by digestion with alkali liquors or with acid sulfites. Other methods in this group depend upon the fact that alcohols and phenols in the presence of an acid catalyst combine with and dissolve the lignin preferentially.

Although the use of concentrated mineral acids to remove the carbohydrates is drastic indeed, the lignins thus obtained are probably closer to the chemical structure of the lignin *in situ* than when removed by solution in alkali or acid sulfite liquors. Lignin can only be dissolved out of the plant material by the formation of an altered product such as an alkali salt of greater complexity than the original lignin or the water-soluble sulphonic acid derivative, lignosulfonic acid, which is obtained as a waste product in the sulphite method of pulping. Even when organic solvents such as phenol or alcohols are employed, the solvent condenses with the lignin.

The two constituent groups in lignin that have

been definitely established are the methoxyl (–OCH₃) and the hydroxyl (OH). The methoxyl content varies with the source of the lignin, the softwood lignins containing about 15% and the hardwood lignins about 21% methoxyl. The presence of hydroxyl groups in lignin is indicated by the fact that it can be acetylated and methylated.[29]

The nature of the lignin molecule is still uncertain. However, it appears likely that lignin is polymerized from building units which are derivatives of phenyl propane, C_6H_5—C_3H_7, since decomposition products obtained by alcoholysis and hydrogenation of lignin have the C_6—C_3 structure.

Hibbert[17] has recently suggested that the precursors of lignin in the plant may be certain aromatic $1:2$ diketones known as benzoins, which act as respiration catalysts. These monomolecular plant catalysts, after completing their primary function, presumably undergo polymerization to the complex lignin products, when they may perform their secondary function of lending strength and rigidity to the plant.

There seems to be considerable evidence that, in the plant, lignin is attached to a carbohydrate, such as a polyuronide. The nature of this possible linkage is as yet undefined.[10, 17, 27]

MICROSTRUCTURE OF COTTON AND WOOD FIBERS

THE study of the microstructure of plants is properly a branch of botany. However, an understanding of the mode of occurrence of fibers in the plant and the arrangement of the fiber elements is essential to an understanding of the chemistry of cellulose. The most important commercial plant fibers are derived from cotton and wood.

Structure of the Cotton Fiber [1, 19]

The cotton plant requires from five to nine months to mature and reach full growth (about 4 feet high). The fruit or boll of the cotton plant, consisting of oval capsules, cracks open about 48 days after the bud forms, exposing the seed hairs or cotton. It may be picked two days after the boll has cracked. Separation of the hairs from the seed is made by "ginning." After this operation a residue of short hairs, known as linters remains on the seed. These are removed by a special delinter machine and are used for guncotton and rayon.

The growth history of the cotton seed hair is

divided into two phases: (1) A period of cell elongation leading to the formation of the primary wall; and (2) cell thickening giving rise to the secondary wall. The first evidence of the formation of the cotton hair is the appearance of a slight swelling on the outer wall of the seed coat on the day of flowering. The swellings elongate rapidly, producing delicate tubular fiber cells on the day after flowering. The full diameter of the mature cotton hair is reached soon after it originates but elongation of the cell continues for 15–20 days and then suddenly ceases.

The cotton hair is a nearly cylindrical single cell about 1200 times as long as it is wide, and containing a lumen or central canal. These hairs are the fibers of commerce. Their growth started two to three days after flowering. The swellings which appear later produce the short-fibered linters in the form of a dense tangled mat which adheres closely to the cottonseed.

During the period of elongation, the protoplasm, or living matter, is enclosed only by the thin primary wall, which is known as the cuticle in the mature fiber. The primary wall possesses a definite skeleton of delicate cellulose threads or fibrils from the first day of its formation. However, this cellulose becomes evident only after removing the associated pectic substances.

The first evidence of the secondary wall appears about the sixteenth day after flowering. The first

secondary deposition stands out prominently after staining, in contrast to the primary wall, as a layer of branching strands or fibrils that wind in a steep spiral around the inner surface of the primary wall. On the following day, another layer of secondary wall is laid down on the inner surface. This deposition continues until a few days before the boll opens, or for at least 25 days. The secondary wall is thus composed of many "lamellae," each representing dense and less dense areas of cellulose. These lamellae become clearly visible when the fibers are swelled (Fig. 1).

A   B
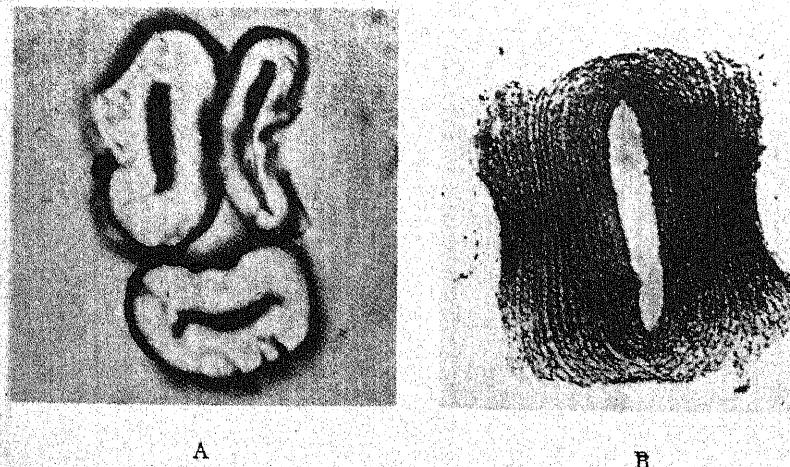
Fig. 1. Cross sections of mature raw cotton fibers. A. Fiber swollen slightly in dilute cuprammonium hydroxide solution. Magnification x 1200. B. Fiber swollen to many times the original diameter to show the lamellate structure. Magnification x 400. (*Courtesy Dr. Milton Harris, The Textile Foundation.*)

When the hair is removed from the seed and dried, the fiber cell collapses into a flat ribbon and twists into a spiral band. These twists or convolutions vary between 150–300 per inch. Their occurrence is largely responsible for the spinning properties of cotton fiber (Fig. 2).
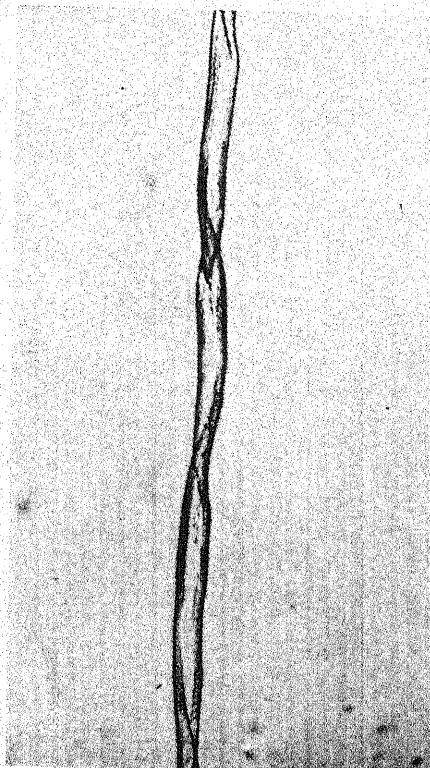

FIG. 2. Mature cotton fiber showing convolutions. Magnification x 180. (*Courtesy Dr. Milton Harris.*)

Cellulose Chemistry

When cotton is treated with curprammonium hydroxide solution, the mature fibers immediately begin to swell, writhe and twist, forming balloon-like structures (Fig. 3). On further action of this
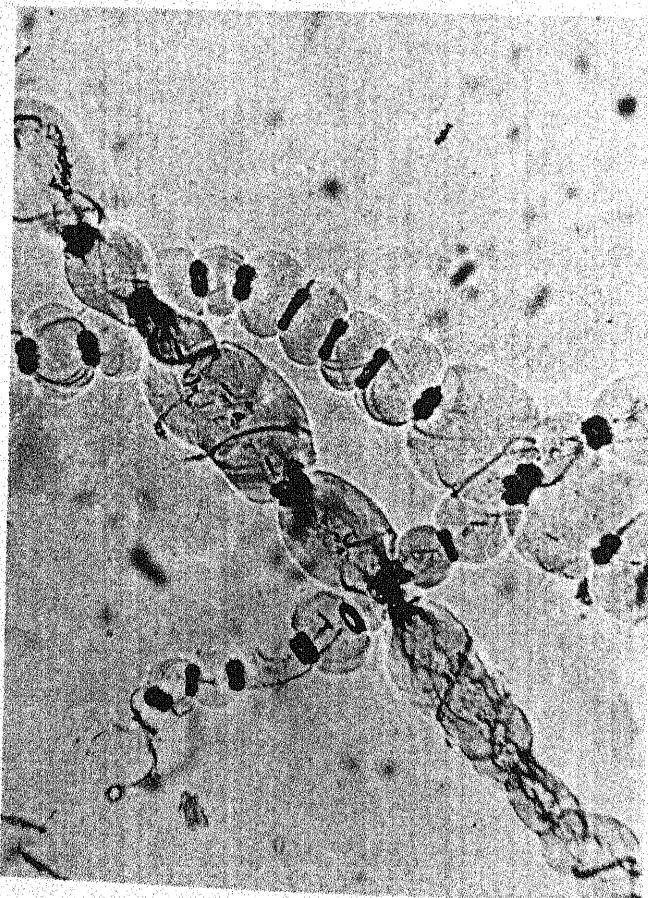

Fig. 3. Cotton fibers in Cuprammonium hydroxide solution, swollen to form balloons. Magnification x 115. (*Courtesy Dr. Milton Harris.*)

reagent, the cellulose dissolves and amorphous fragments from the primary wall and lumen area remain as residue. The characteristic balloon formation of cellulose fibers has frequently been described as due to the rupturing of the primary wall into a series of constriction bands which restrain the expanding cellulose. However, it was recently found that even after removing the pectic substances from the primary wall, balloon formation was observed. It has, therefore, been suggested that the irregular swelling along the fiber axis which results in balloon formation is dependent in part on the orientation of the fibrils in the secondary wall and in part on the constricting influences of the primary wall.

The fibrils, of which the lamellae are composed, are orientated at an acute angle with respect to the axis of the fiber. The fibrilar windings make either an "S" or a "Z" twist, reversal of direction taking place many times in a single fiber. The orientation of the fibrils is such that if the winding in one layer makes an S twist, the fibrils immediately beneath make a Z twist. The directions of these windings follow the direction of the convolutions and thus explain their occurrence in the free fiber.

The fibrils may be picked apart by micromanipulative methods, yielding long slender hairlike units. The fibrils in turn may be degraded to yield still smaller units. However, the existence of the fibrils and other microscopic units as structural elements of the fiber is not at all certain. They may be merely planes of physical or chemical weakness yielding dis-

sected fragments of the coherent matrix of cellulose.[18, 31]

Microstructure of Wood Fibers [4]

Wood fibers have a structure somewhat similar to that of cotton, except that the cells are bound
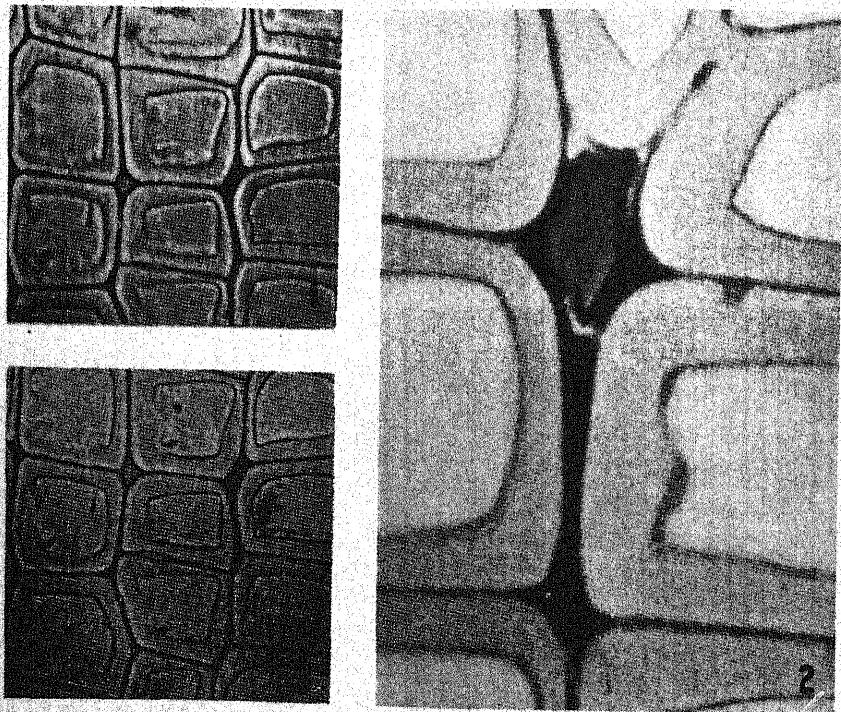

Fig. 4. Cross sections of white pine wood. 1. Photographed on infrared film after staining with a dye which absorbs infrared radiation. Magnification x 540. 2. The same; magnification x 1500, showing the component parts of the middle lamella, i.e., the intercellular substance and the adjacent primary walls. 3. The same section photographed on ordinary panchromatic film. Magnification x 540. (*Courtesy of Dr. William M. Harlow, The New York State College of Forestry.*)

together by a non-cellulosic material. This amorphous material in the middle lamella or intercellular layer is chiefly composed of lignin together with a smaller proportion of hemicellulose, and perhaps a very small amount of cellulose. Besides acting as a cementing material for the cells, the middle lamella lends rigidity and strength to the wood structure. In contact with the middle lamella is the thin primary wall of the cellulose fiber. This is composed chiefly of cellulose with some hemicellulose. As in the cotton fiber, most of the cellulose of the wood



A   B
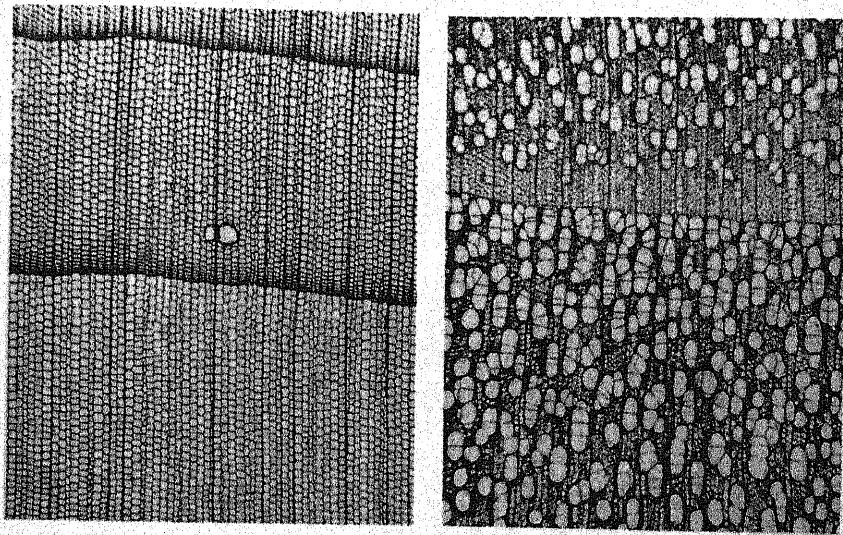
FIG. 5. Cross sections of typical evergreen and deciduous woods. A. Cross section of Engelman spruce. B. Cross section of Aspen wood. Magnification x 50. (*Courtesy of Dr. Harry F. Lewis, The Institute of Paper Chemistry.*)
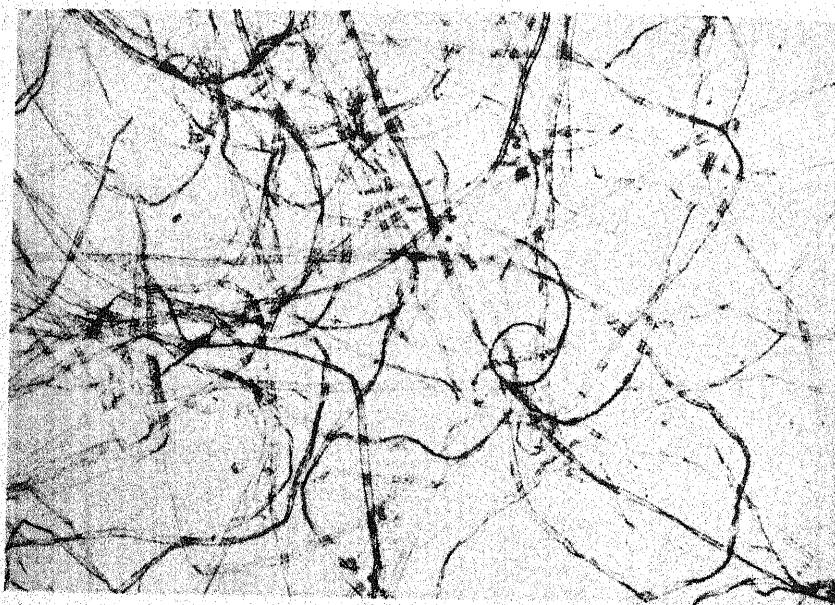
Fig. 6. Papermaking fibers from Gampi (similar to the more common wood fibers). Magnification x 100. (*Courtesy Dr. Harry F. Lewis.*)
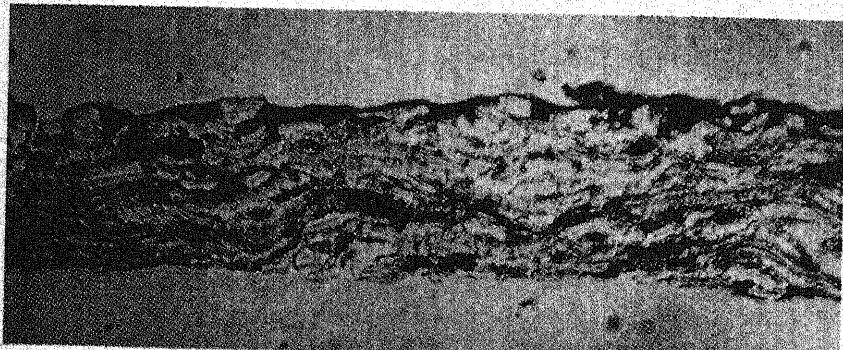

FIG. 7. Cross section through a sheet of printed handmade paper. Various sections of the individual fibers are shown interspersed with the loading of filler (in this case calcium carbonate) which printing papers always carry. The ink on the surface is shown as an irregular black line. Magnification x 350.

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fiber is located in the secondary wall. In wood, however, the secondary wall contains a small amount of hemicellulose and lignin and has only about 5–10 concentric layers. Wood fibers mature much more rapidly than cotton fibers (Figs. 4 and 5).

Wood cells are of various shapes according to their function in the plant: fibers, tracheids and vessel segments for the upward transport of water; wood parenchyma and ray cells for the transport and storage of food products and the secretion of resins. From the standpoint of cellulose technology, we are interested particularly in the fibers and tracheids whose thickened cell walls have developed the secondary function of lending support to the woody plant. On removing the noncellulosic intercellular bonding material the fibers are separated from one another and retain their original shape. These fibers are the basis of most paper (Figs. 6 and 7).

ISOLATION AND PURIFICATION OF CELLULOSE

THE general methods of isolation and purification of cellulose may be divided into four fundamentally different groups depending on the source of the plant product: (1) Seed hairs such as from the cotton plant, (2) Bast fibers occurring in the inner bark of certain fibrous plants, such as flax, (3) stem fibers such as occur in straw and esparto, and (4) woody plants.

Fibrous Plants

Cellulose occurs alone in a relatively pure condition only in the seed hair of the cotton plant. The impurities of cotton consist of small amounts of pectic substances, cotton wax, albuminous matter, and inorganic salts. By mild and careful purification with the absolute exclusion of all air it is possible to preserve nearly the original length of the molecular chain and to prevent side reactions. For this reason, carefully purified cotton cellulose has formed the starting material for most of the re-

searches on the constitution and properties of cellulose.

The fatty material is removed by boiling in dilute alkali solution containing rosin soap. It is then washed with hot water and again with dilute alkali. These operations are repeated several times. It is then washed thoroughly with cold water, bleached with dilute sodium hypochlorite solution, washed with distilled water to remove all traces of chlorine and dried in the air. This "standard cellulose" commonly contains less than 0.05% ash and about 99.8% alpha-cellulose.[2]

The preparation of bast fibers from flax is based on methods practised since ancient times. Only the main stalks are utilized, the branches, leaves and seeds being removed by a series of forks. The straw is tied in bundles and subjected to a process of retting, or a pectin fermentation, for the purpose of separating the woody matter enclosing the fibers. The retted flax is passed through rollers to break up the woody material, making it suitable for the next operation of "heckling." This is a combing operation in which the long fibers are arranged parallel and the short fibers removed. The waste is known as tow and is used for making twine. The flax straw contains about 27% of flax fiber. The fiber is nearly 80% pure cellulose.[16]

Esparto is not used to any great extent in this country, but in Great Britain it is one of the most important fibrous raw materials. This grass is im-

ported from Spain and Africa in large quantities. After removing dirt and sand, it is pulped in stationary digesters with 16–18 pounds of 70% caustic soda solution per 100 pounds grass for 2–6 hours at 5–50 pounds steam pressure. The cooked pulp is then thoroughly washed and bleached. Esparto pulp is used extensively in printing papers. The bast fibers are short and narrow, cylindrical in cross-section with a small central canal and taper off at the ends to fine points. These characteristics result in a smooth paper surface which faithfully reproduces fine details of printing.
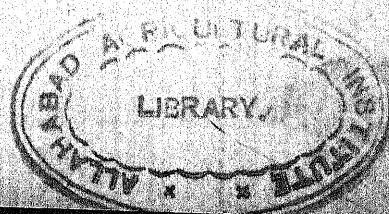
Woody Plants

The woody plants contain about 50–60% of cellulose, the separation of which is much more difficult and involved than in the case of the annual fibrous plants. The other 40–50% of the wood consists chiefly of the encrusting materials, lignin, and hemicelluloses, requiring hydrolyzing conditions before they may be removed.

The most reliable laboratory method is that of Cross and Bevan, essentially the same as worked out by these pioneers of cellulose chemistry more than sixty years ago. The method consists in subjecting the moistened plant material to the action of chlorine gas and then removing the reaction products with a hot solution of sodium sulphite. Four to five chlorinations are generally required to ob-

tain a uniformly white residue of cellulose pulp, free from residual lignin and which does not develop a pink or brown coloration on treatment with sodium sulphite solution.

The resultant Cross and Bevan cellulose contains some pentosan or furfural-yielding material and cellulose fractions of a low degree of polymerization which are soluble in 17.5% sodium hydroxide solution (known as Mercer's solution). To separate these components, the cellulose is triturated with mercerizing solution and filtered. The insoluble residue is called alpha-cellulose. It is comparable in its properties to cotton or other resistant cellulose. On acidification of the filtrate, a precipitate is obtained which is filtered, washed and weighed as beta-cellulose. The material that is soluble in both alkali and acid solutions is gamma-cellulose. It is determined by difference.

Industrial Pulping

The separation of cellulose on a large scale from woody plants is the basis of the pulp and paper and rayon industries. The most important industrial methods are the sulphite, soda, and sulphate processes. For each process the digestion liquor, the conditions of digestion, the species of wood used and the pulp obtained are different. The general scheme of treatment, however, is the same.

The clean pulpwood is reduced to chips varying

in size from five-eighths to 1½ inches depending on the method of digestion. These are screened to assure uniformity and to eliminate dirt and sawdust. The chips are charged into pressure digesters holding 15 tons or more of wood. Fresh liquor is added and the charge is cooked for a predetermined time at a definite elevated temperature and pressure. The process of cooking converts the lignin and the polyuronides of the middle lamella to a derivative or hydrolysis product which is soluble in the digestion liquor. The chips are softened, thereby, during cooking, but the fibers still hold together in large bundles. To produce the pulp in which each fiber is separated from its neighbor, the pressure in the digester is reduced gradually to about 50 pounds and the charge is blown violently into a blow pit. The suddenly reduced pressure causes the disintegration of the fiber bundles. The blow pit is provided with a false bottom allowing the waste liquor to drain. This liquor contains most of the noncellulosic portion of the wood as well as the residue of the cooking chemicals. After draining off the liquor, the pulp is washed thoroughly with water.

The resulting product is unbleached pulp still containing much of that portion of lignin occurring in the cell wall proper. For the production of fine paper or for further purification to "dissolving pulp" for use in rayon manufacture, the pulp is then bleached. The bleaching agent is chlorine or calcium hypochlorite (CaCl.OCl) which in solution

forms hypochlorous acid (HClO). The function of the bleaching agent is two fold, i.e., to form a derivative of lignin which is soluble in alkali and to oxidize the non-cellulose portions of the pulp. Bleaching is sometimes carried out in two or more stages using chlorine water and alternating with an alkaline and water wash. Bleaching is then completed by oxidation with hypochlorite solution and thorough washing with water.

Sulphite Process

The sulphite process constitutes the most important method of pulping. The cooking liquor is commonly a mixture of free sulphurous acid and calcium bisulphite. The liquor acts both as an acid and as an addition compound. As an acid it hydrolyzes the hemicelluloses and less resistant portions of the cellulose into the corresponding water-soluble sugars. As an addition compound it reacts with lignin to form the water-soluble sulphonated lignin derivative. The exact composition of the liquor varies with the particular process in a given mill. A typical digestion liquor has a total sulphur dioxide content of 5.85–6.20 per cent, of which 1.05–1.15 percent is combined as bisulphite $(Ca(HSO_3)_2)$. The spent liquor from the sulphite process, known as waste sulphite liquor, is not recovered. It is commonly discharged into the nearest stream.

Sulphate Process

The sulphate or kraft process is used chiefly for the pulping of resinous soft woods. The active agents are sodium sulphide (Na_2S) and sodium hydroxide ($NaOH$). In contradistinction to the sulphite process, the spent digestion liquor from the sulphate process, known as "black liquor," is recovered and used to make up fresh liquor.

The sulphate process gets its name from the fact that sodium sulphate (Na_2SO_4) is used to make up the loss of chemical during recovery. Sodium sulphate itself is relatively inert insofar as its action on wood is concerned. But during recovery it is reduced by the carbon to sodium sulphide (Na_2S).

The process of recovery involves the evaporation of the black liquor to about 50% solids. It is then incinerated producing free carbon and sodium carbonate. This black ash is fed into a blast furnace where the carbon is completely burned. The mixture of salts, consisting mainly of sodium carbonate and sodium sulfite, is then discharged in a molten form into a dissolving tank. The resultant solution is causticized with lime, thus converting the sodium carbonate to sodium hydroxide. After filtration the concentration is adjusted and this liquor is then ready to be used for the digestion of a fresh batch of wood chips.

Soda Process

The soda process also depends on an alkaline digestion liquor, namely caustic soda, for defibration. It is used for the pulping of hardwoods, such as poplar, maple and gum. Digestion is carried out with 6–8% sodium hydroxide solution (the amount being about four times the weight of the wood) by cooking for 6–10 hours at 150–180°C.

The "black liquor" of the soda process is also recovered in a manner similar to that of the sulphate process. After evaporation and incineration of the concentrated liquor, the resulting black ash is leached with hot water to dissolve the sodium carbonate. This solution is then caustisized with lime to form sodium hydroxide for fresh digestion liquor:

$$Na_2CO_3 + Ca(OH)_2 = 2\,NaOH + CaCO_3.$$
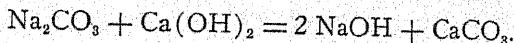
GENERAL PROPERTIES OF CELLULOSE

CELLULOSE is a typical colloidal substance with an internal surface in the swollen state of about 3,000,000 square centimeters per gram.[35] As a colloid its properties are mainly those that are determined by the chemistry and physics of large internal surfaces, such as absorption, swelling, dissociation, coagulation, ultimate structure and optical properties. In this chapter we shall consider sorption of water vapor and optical and electrical properties of cellulose.

Sorption of Water Vapor

The moisture content of cellulose products varies with the amount of moisture in the atmosphere. When the relative humidity is gradually increased, the rate of increase of water adsorption by the cellulose decreases to a minimum at about 80% relative humidity and then increases to a maximum at the fiber-saturation point. A characteristic sigmoid curve is thus obtained. When the process is reversed, decreasing the relative humidity until the sample is again dry, a similar curve is obtained.

30

These two curves never coincide. Desorption always shows higher moisture content values than adsorption for the same equilibrium relative humidities. This phenomenon is called *hysteresis*.
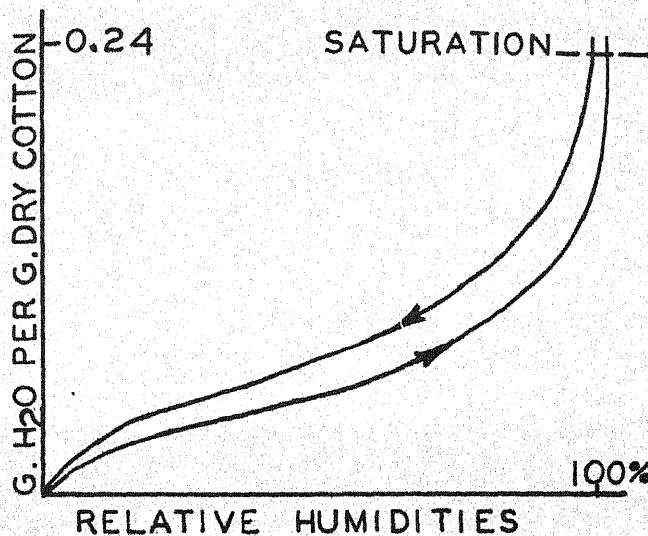

FIG. 8. Hysteresis curves for cotton.[87]

The most plausible explanation for this effect involves the secondary valence forces (hydrogen bonds) of the hydroxyl groups of the cellulose molecules. In the original water-soaked condition the hydroxyl groups are practically all satisfied by water. When the cellulose is dried, the freed hydroxyl groups from adjacent cellulose molecules mutually satisfy each other. Upon increasing the

relative vapor pressure, part of the hydroxyl groups that have mutually satisfied each other are not free for water adsorption, thus giving a decreased adsorption. Above 80% relative humidity, particularly near the fiber saturation point, more hydroxyl groups are free, thus giving an increased rate of adsorption. Finally a condition is reached in which the hydroxyl groups are again practically all satisfied by water.

It is very difficult to dry cellulose completely. Thus, cotton dried in vacuum over phosphorus pentoxide still retains 0.35% water. This water can be removed by raising the temperature to 100°C., but it will be readsorbed on cooling. Cellulose is thus a more powerful dehydrating agent than phosphorous pentoxide.[39]

Optical Properties [34]

The double refraction of a *macro*crystal is due to the different atomic spacings in the different structural directions of the crystal lattice allowing light to pass with different velocities. In the case of cellulose a single crystallite cannot be observed. The optical effects are, therefore, composite. Orientation in a single fiber occurs only in the fiber direction. It is, therefore, impossible to distinguish more than two refractive indices. The difference between the axial and the transverse refractions is

taken as a measure of the double refraction although the orientation of the structural units may not always be exactly axial or transverse.

The double refraction of cellulosic materials is made up of a combination of three different double refractions, any one or all of which may be effective in a given case. The internal double refraction is similar to that exhibited by macrocrystals and is due to an anisotropic arrangement of atoms within the molecule. The particle double refraction is due to the anisotropic arrangements of the structural, micellar units, the dimensions of which are less than the wave-length of light. The third type is a special form of double refraction which is exhibited only when the material is under a stress.

The double refraction is measured by the method of disappearance of the fiber from view in a liquid of equal refractive index in the direction parallel and perpendicular to the fiber axis. Ramie fiber, which has the most perfect orientation of any known natural fibrous material, has an axial, transverse and double refraction of 1.596, 1.528 and 0.068. All other cellulosic fibers with a high degree of micellar orientation, such as flax, have similar values. Cotton and other forms of cellulose with less perfect orientation of micellar structural units give lower axial refractions and higher transverse refractions, resulting in lower double refractions, for example 1.578, 1.532 and 0.046 respectively.

This is due to the elliptical wrapping of the fibril structure about the fiber axis of cotton. Calculating the axial refraction on the assumption of perfect axial alignment (or of a single fibril) a value of 1.596 was obtained which is practically the same as for ramie.

Electrical Properties

Dry fibrous materials are in themselves good electrical insulators. But since it is practically impossible to prevent them from adsorbing moisture, their conductivity depends to a large extent on their moisture content. The conductivity increases very rapidly with an increase in moisture content up to the fiber-saturation point and then drops off sharply. Thus the electrical conductivity of wood increased over a hundred thousand fold in the range from seven to thirty percent moisture. On further increasing the moisture to 300 percent, the conductivity increase was only about twentyfold.[34]

The electrokinetic phenomenon known as the "zeta potential" is characteristic of cellulose and other colloidal materials. Any solid in contact with a liquid assumes an electrical charge with respect to the liquid as a result of selective adsorption of ions. The oppositely charged ions become immobilized in the bulk solution in close proximity to the adsorbed ions in order to maintain electrical neutrality. The electrokinetic potential difference set

up between the adsorbed ions and the bulk of the solution is the zeta potential. Cellulose has a negative zeta potential with respect to water and it is of the magnitude of 10–20 millivolts.

DISPERSION OF CELLULOSE

CELLULOSE can be dispersed in only a few aqueous media of certain concentrated solutes. The solvent has to overcome the secondary valence forces between the main valence chains, and in addition it must be a dispersing agent for these long chains which have a molecular weight of the order of 500,000. It is questionable whether cellulose in dispersion ever exists in the native form. Cellulose regenerated from its dispersion is always a modified form known as "hydrate cellulose." It has an expanded crystal lattice and also an increased sorptive power. Chemical changes may also take place, such as partial hydrolysis or partial oxidation resulting in shorter average chain length. The former type is known as "hydrocellulose" and the latter as "oxycellulose." There is really no "solvent" for cellulose in the usual sense of the term. The "solvent" is really a dispersing reagent which has a strong enough affinity for the cellulose chain molecule to overcome the secondary valence forces which hold these chains together. This reagent reacts with the cellulose to form a derivative, or, since we are not certain of the composition of this new substance,

we may loosely call it a complex. It is this new cellulose complex which then disperses in the reagent. The corollary to this explanation is that the reagent has disrupted the secondary valence forces holding the crystallite together, and that cellulose exists in dispersion mainly as the single long chain molecule, that is, forming a monodisperse solution.

Cuprammonium Solvent

One of the oldest and most important discoveries in cellulose chemistry occurred when Schweizer in 1857 noted that cellulose was soluble in an ammoniacal copper solution containing the complex base $Cu(NH_3)_4(OH)_2$ and that the cellulose could be regenerated from such a solution in an unchanged chemical form.

A viscosity determination of cellulose in "Schweizer Solution" is of great technical importance in evaluating the origin and previous history of a cellulose sample. Raw cotton shows the highest viscosity, wood celluloses usually have much lower viscosities, while degraded and regenerated cellulose give the lowest viscosities. The higher the concentration of copper in the cuprammonium solution the greater is the solvent power for cellulose. Because of this variable, the solvent concentration is accurately standardized when used as a routine test for estimating the extent of chemical degradation in technical processes. Thus, to determine the

strength of cotton goods, the viscosity is measured in a solution containing 15 grams copper and 240 grams ammonia per liter and sufficient cotton to give a 0.5% solution. The tensile strength decreases with decreasing viscosity of the solution or with increasing "fluidity" which is the reciprocal of viscosity. The best cotton has a fluidity of 1–5 and bleached cotton 5–10. Fluidities of 20–30 indicate chemical degradation of cotton, while most rayons gives figures of 40 or more.[24]

The modern method of manufacturing artificial silk, or rayon, by the cuprammonium or Bemberg process results in filaments that are 2.5 times finer than those of natural silk. The beaten cellulose is mixed with freshly precipitated cupric hydroxide to form a product which is soluble in concentrated ammonia. After treating for 24 hours in a dissolving tank, a concentrated solution of cellulose is obtained which is diluted to 7–8% with aqueous ammonia and is then used for spinning. The solution is forced through spinnerets into a feebly coagulating bath of water. The incompletely coagulated filaments are stretched by a mechanical device until they are of the required fineness and are then coagulated completely in a second bath of dilute sulphuric acid.[7]

Dispersions of cellulose in cuprammonium solvent are unstable in the presence of even slight amounts of oxygen. When the greatest precautions are taken to exclude oxygen and if the time of contact is short, no chemical degradation of the cellu-

lose occurs. Cuprammonium hydroxide comes the closest to being a true physical solvent for cellulose, or strictly speaking, for the compound formed between cellulose and cuprammonium. Cellulose regenerated from cuprammonium solution is in the "hydrate" state. The freshly precipitated cellulose is dispersible in two normal sodium hydroxide solution, but loses this property on standing.

Quaternary Compounds

Cellulose may be dissolved in 2.3–4.0 normal tetraethyl ammonium hydroxide, 2.1–3.6 normal trimethyl paratolyl ammonium hydroxide and 1.7–2.4 normal tributyl ethyl ammonium hydroxide. At concentrations below or above these, only swelling occurs. Other strong organic bases reported to be solvents for cellulose are the corresponding tetraalkyl phosphonium and arsonium and trialkyl sulphonium and selenium bases. The best solvent power is exerted by these quaternary compounds within a narrow range of concentration, above or below which only swelling occurs.[21]

Acid Solvents

Concentrated sulphuric, hydrochloric and phosphoric acids act as solvents for cellulose. However, on account of the strong tendency towards hydrolysis, the acid has to be cooled and the time of contact

be made short. Paper is parchmentized industrially by passing it through 78% sulphuric acid at 10°C. for 15 seconds, followed by immediate washing. 40% hydrochloric acid and 84% phosphoric acid will dissolve cellulose, from which it can be reprecipitated quantitatively by the addition of water. These acids will dissolve "hydrate cellulose" and partially degraded cellulose at lower concentrations than is required to dissolve native cellulose.

Salt Solvents

The degree of solubility of cellulose in neutral salt solutions is a function of the degree of hydration of the ions and increases with it. The hydration of cations and anions is additive so that the solubility in any salt may be calculated according to a series of decreasing hydration of the ions:

$$Ca > Sr > Ba$$
$$Li > Na > K > NH_4$$
$$CNS > I > Br > Cl > No_3 > \tfrac{1}{2}SO_4.$$

These series are practically the same as the lyotropic series. The most hydrated ions are solvents for cellulose while the less hydrated cause swelling. A calcium thiocyanate solution is an efficient solvent for cellulose provided it is of such a concentration that it boils between 135–150°C., has a positive heat of dilution not greater than 3,500 calories, and a viscosity at least 3.3 times that of water at 20°C.

The cellulose precipitated from such a solution has the general properties of regenerated or hydrate cellulose although it is somewhat more degraded than a similar product from cuprammonium solution.

Mercerization [25]

While filtering sodium hydroxide solution through several layers of cotton cloth, John Mercer in 1844 noted a decrease in alkali content in the filtrate. Systematically following up this observation he found that treatment of cotton with 17.5–18.0% sodium hydroxide resulted in a contraction in the direction of fiber length of about 20–25%, an increase in strength of 40–50%, and an improvement in dye absorption. However, modern "mercerizing," which has become technically very important, is carried out chiefly to increase lustre and secondarily for its effect in increasing the affinity for dyestuffs. A method to increase lustre was discovered and patented by Lowe in 1889. The material is mercerized under tension. Two methods are followed in this treatment: (1) Shrinkage of the cloth in about 23% alkali followed by stretching and (2) continuous application of tension while the cloth is being treated without any shrinkage taking place.

When the cotton fiber is mercerized without tension, its characteristic convolutions and flat ribbon-like form disappear. It becomes rounder, smoother
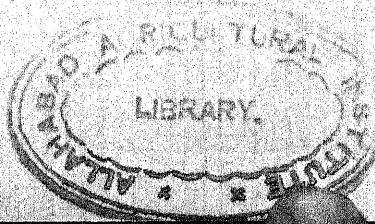
and more uniform. When mercerized under tension, the fiber becomes perfectly cylindrical. The original kidney-bean shape of the cross-section and the long, narrow slit of the lumen change to a circle with the lumen often appearing only as a central point.

The question as to whether sodium hydroxide forms a chemical compound with cellulose has received conflicting replies beginning with Mercer himself in 1844. Based on X-ray evidence this may now be explained by a chemical reaction. With concentrations of alkali below about 10%, the solution is absorbed only in the amorphous fringes of the micelle, no change in the X-ray lattice takes place, and therefore no chemical reaction occurs. As the concentration of the alkali is increased, the interior surface of the micelle becomes more and more available and surface reaction increases. Under conditions of optimum swelling, when all the internal surface becomes available, the addition of alkali may be considered as a true chemical reaction, although each glucose anhydride unit in the cellulose chains probably does not react to the same degree. The number of NaOH molecules held probably varies along the chain.

The alkali cellulose formed by reacting cellulose with strong aqueous solutions of caustic soda has a definite crystal lattice as measured by X-rays. On washing out the alkali to obtain the mercerized cellulose, a third crystal lattice is obtained which

is of the expanded type of hydrate cellulose. The expanded crystal lattice explains the greater chemical reactivity of mercerized cellulose. If the fibers are stretched in the swollen state, the long chain molecules arrange themselves parallel, the secondary valence forces are brought into play, the crystallinity is increased and consequently the strength is increased.

The Viscose Process

In 1892, Cross, Bevan and Beadle discovered that alkali cellulose reacted with carbon disulphide to give a product soluble in dilute sodium hydroxide solution from which the cellulose with its original properties could be regenerated by acidification. This discovery was of very great technical importance, leading to the development of the "viscose" process of rayon and cellophane manufacture.

The general reaction is as follows:

$$R.OH + NaOH = R.ONa + H_2O$$
cellulose
$$R.ONa + CS_2 = R.OCS.SNa$$
Cellulose xanthate
$$R.OCS. SNa + acid = CS_2 + R.OH + Na \text{ salt}$$
Regenerated cellulose.
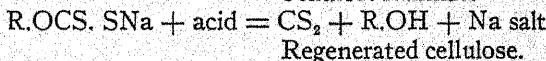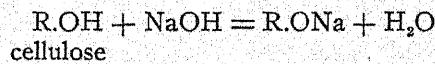
The manufacture of viscose involves the following steps: Alkali cellulose is formed by the action of 17.5–18.5% sodium hydroxide solution on pulp sheets. The liquor is drained from the impregnated

swollen sheets and excess solution removed by pressing. Alkali cellulose having a ratio of $2 C_6H_{10}O_5 : 1 NaOH$ is formed. The alkali cellulose is shredded into light, fluffy crumbs and allowed to mature for 48–72 hours. During this time oxygen is probably absorbed and partial depolymerization of the cellulose takes place. The crumbs are then churned with an amount of carbon bisulfide corresponding to a ratio of $1 CS_2 : 1.25–1.5 C_6H_{10}O_5$. The yellow color of the syrupy mixture gradually changes to orange-red and then to brown-red. The unreacted carbon bisulfide is removed and sufficient water and sodium hydroxide added to produce a solution containing 7–8% cellulose and 6.5–7% sodium hydroxide. The solution is ripened for 4–5 days, filtered, and stored in a vacuum for 24 hours to eliminate gas bubbles.

During the ripening the viscous brown solution at first decreases in viscosity to a minimum, then rises gradually and finally increases very rapidly just before jelling. At the time of solution a compound is formed having the ratio of 1–2 glucose units per xanthate group. The compound $(C_6H_{10}O_5$ —$C_6H_9O_4$—$OCSSNa)_x$, has been isolated by several investigators and is considered most nearly to represent unripened cellulose xanthate. During the ripening process the ratio of carbohydrate gradually increases until, if allowed to proceed to the stage of gel formation, it would be completely regenerated cellulose. As the sodium cellulose xan-

thate gradually decomposes, the regenerated cellulose formed is dispersed in the undecomposed xanthate.

The viscose solution is spun through a spinneret into an acid bath causing coagulation and decomposition of the remaining cellulose xanthate. Each spinneret has 10–40 fine openings. Each opening forms a filament and all the filaments from one spinneret are united to form the thread or fiber. The fiber is washed, reeled, twisted and dried under tension and the sulphur from the coagulated fiber is removed by treating with 1% sodium sulphide. The fiber is bleached with a solution of hypochlorite and is finally washed, oiled and dried without tension at 40–60°C.

For the production of cellophane,[30] the viscous mass is diluted with NaOH solution and a film is cast through a nozzle having a long slit as an orifice. The extruded film is deposited on a fabric belt. It is carried through a solution of ammonium sulphate where it is coagulated and hardened and then through baths of sodium chloride solution, dilute sulphuric acid, and water. If the sheet were dried at this time, it would be very brittle. It is, therefore, passed through a bath of glycerine where the sheet picks up about 7% of this hygroscopic agent. This serves to keep moisture in the sheet, acting as an effective plasticizer. Moistureproof cellophane is made by passing it through a solution of low viscosity plasticized cellulose nitrate.

DERIVATIVES OF CELLULOSE

As a compound containing three hydroxyl groups for each anhydroglucose unit, cellulose is capable of forming esters with acids and ethers with alcohols:

$$[C_6H_7O_2(OH)_3]_n + 3\,n\,AcOH =$$
$$[C_6H_7O_2(OAc)_3]_n + 3\,n\,H_2O$$
$$[C_6H_7O_2(OH)_3]_n + 3\,n\,ROH =$$
$$[C_6H_7O_2(OR)_3]_n + 3\,n\,H_2O$$
$$\text{Example}: AcOH = CH_3COOH \text{ and } ROH = C_2H_5OH$$
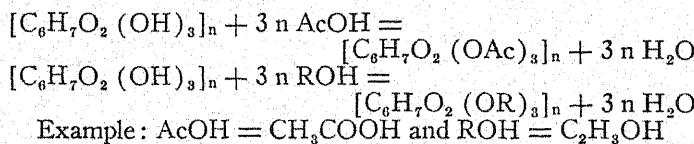
In general all methods for the preparation of ethers and esters with simple alcohols are applicable to cellulose. This is rather unexpected since cellulose is insoluble in the reaction mixture. However, the reaction is topochemical, that is, a surface reaction working into the interior of the fiber wall. The reaction is also heterogeneous in the sense that not all the hydroxyl groups on all the glucose units react uniformly, nor completely, except when the fully substituted derivative is formed.

Esters of Nitric Acid

The general method of preparation of cellulose nitrate with a mixture of nitric and sulphuric acids

was discovered by Braconnot in 1833. Schoenbein, in 1845, was the first to prepare the trinitrate and put it to technical use as an explosive. The function of the sulphuric acid is believed to be that of absorption of water of reaction, thus favoring the introduction of a larger percentage of nitrate groups. The amount of water in the nitration mixture bears an inverse relation to the degree of nitration obtained, since the reaction reaches an equilibrium.

A completely nitrated cellulose, corresponding to three nitrate groups for each $C_6H_{10}O_5$ unit would contain 14.14% nitrogen. But cellulose nitrates containing much over 13.1% nitrogen are very unstable. All the nitrates of cellulose are readily flammable.

The most highly nitrated cellulose is guncotton. It is prepared by treating dried purified cotton linters with about 30 times their weight of a mixture of 75% H_2SO_4, 15.75% HNO_3, 1.30% HNO_2, and 7.95% water at 15°C. for 3–12 hours. The nitrated cellulose is washed with cold water and then with boiling water. The crude nitrate is contaminated with small amounts of cellulose sulphate, hydro- and oxycellulose and certain non-cellulose nitro compounds. In this state it is subject to spontaneous decomposition and the careful removal of impurities is essential. This is accomplished by the "stabilization process." This process consists of first boiling the impure guncotton in weak acid solution. Then it is treated with boiling water containing

calcium carbonate. After centrifuging to remove most of the water, the cellulose nitrate is treated with alcohol in a press to displace the remaining water; then it is washed with ether to remove most of the alcohol. The alcohol-ether is finally removed with hot air.

The fibrous form of guncotton burns quickly but quietly in the open. When detonated in a confined space it explodes with great violence. By gelatinization with solvents containing a plasticizer and stabilizer, the forces of the explosion are moderated and the nitrate may be used as a high explosive. When partially dissolved in nitroglycerine and mixed with castor oil or other plasticizers, such as dibutyl phthalate, it forms a gelatinous mass known as smokeless powder. When this powder decomposes, NO_2 fumes are given off which react with moisture to form nitric acid. The acid in turn catalyzes the decomposition of cellulose nitrate. It is the function of the stabilizer to stop this chain reaction. It reacts with the free NO_2 and thus removes it.

Guncotton is soluble in acetone and ethyl acetate, but is insoluble in methyl alcohol or ether-alcohol. When cellulose is steeped with an acid mixture of 55% H_2SO_4, 17% HNO_3, and 28% water at 45–55°C. a cellulose nitrate is formed with a nitrogen content of less than 12.5%. A solution of these lower cellulose nitrates is known as collodion or pyroxylin. These names are applied to all cellulose

nitrates which are soluble in amyl acetate, methyl alcohol or ether-alcohol. Cellulose nitrates containing 11.5–12.5% nitrogen are used for the preparation of photographic films, while compounds with 10.5–11.5% nitrogen are used for the manufacture of celluloid plastics.

Camphor is the standard plasticizer for cellulose nitrate plastics. The alcohol-wet cellulose nitrate is mixed with plasticizers and solvents and strained under hydraulic pressure while in a soft condition. It is colored and freed from volatile solvents by sheeting on rolls. It is then baked under pressure into cakes slightly larger than the standard 20 x 50 inch size accepted by the trade. It is sheeted by slicing, seasoned to remove solvents and is finally press-polished under low heat. It may also be extruded continuously as tubes, rods or sheets.

These involved operations are required because of the susceptibility of the plastic to high temperatures. During the last few years it was found that careful treatment to remove the last traces of sulphate have resulted in a surprising stability. The high flammability may also be reduced by special plasticizers containing chlorine or phosphorous as fire retardants.

The viscosity of the cellulose nitrates in solution is of the greatest technical importance. The viscosity depends on the extent of breakdown of cellulose chains into shorter units. Low viscosity cellulose nitrates, corresponding to a degree of poly-

merization of about 175 (which are required for the manufacture of lacquers) are obtained from a modified form of cellulose which may range from mercerized to slightly hydrolyzed or oxidized cellulose. The great advantage of the low viscosity cellulose for this purpose is the ability to produce lacquers with high solids concentrations. Fewer applications and less drying time for each application are needed. The higher viscosity nitrates, corresponding to a degree of polymerization of 500–600, are suitable for artificial leather, airplane dopes and various cements. For the preparation of gelatinous explosives, it is essential to use cellulose of the highest viscosities, corresponding to a degree of polymerization of the order of 3,000, or of the enormous molecular weight of about 750,000.[30]

Cellulose nitrate may also be used for the manufacture of rayon. This is, in fact, the oldest method for the manufacture of artificial fiber, having been first successfully developed by de Chardonnet in 1884. The method involves nitrating cellulose to a nitrogen content of 11.2–11.7% so that it is soluble in a mixture of equal parts of ether and alcohol. The viscous solution is forced through fine openings into a current of warm air which removes the solvent and leaves a filament of cellulose nitrate. Some 10–25 filaments are combined to form a thread. The threads are denitrated by treating them in a solution of sodium or ammonium acid sulphide. This results in regeneration of cellulose and a drop in

nitrogen content to a minimum of 0.05%. The loss in weight is about 30% and the loss in tensile strength about 25%, but the rayon is now as soft as natural silk and has lost its high flammability.[7] This process is no longer used in the United States.

Esters of Acetic Acid

The fully substituted cellulose triacetate, known as the "primary acetate," is easily prepared. The general commercial practice is to acetylate cellulose with acetic anhydride in the presence of a small amount of sulphuric acid (as a catalyst) and in the presence of glacial acetic acid (to dissolve the triacetate produced). The primary acetate is insoluble in acetone, but is soluble in chloroform, aniline, acetic acid, and other solvents. It is resistant to boiling water, but the threads and films formed from it are weak and brittle. These properties render it unsuitable for commercial purposes.

In 1903, Miles discovered that partial hydrolysis of the primary acetate resulted in the production of a secondary acetate soluble in acetone and other solvents, but insoluble in chloroform, and having greatly improved technical properties. The primary acetate must be made first, since the acetylation equilibrium reaction is not reversible like the nitration reaction. This product is then partially hydrolyzed by means of acetic acid and water to the secondary acetate with 51–57.6% acetic acid

content, corresponding to about 2.5 acetyl groups per $C_6H_{10}O_5$ unit.

The explanation for the low strength of the primary acetate and the improvement on partial hydrolysis is furnished by the micellar theory. The micelle is the part of the cellulose structure which lends tenacity to the fiber. The cellulose chain molecules are held together in the micellar region, in a direction at right angles to the fiber axis, by secondary valence forces exerted through the free hydroxyl groups. When these hydroxyl groups are completely substituted by acetyl groups, the secondary valence forces are greatly reduced and slippage of chain molecules occurs to yield low strengths.

For the production of rayon, the secondary acetate is dissolved in acetone and allowed to ripen until the desired physical properties such as the solubility of the final product, are obtained. The secondary acetate is then precipitated in the form of white flakes by pouring the solution into an excess of cold water. The purified material is washed, centrifuged and dried at 20–30°C. It is dissolved in acetone, filtered and kept under vacuum until all air is removed. The cellulose acetate is then spun into continuous filaments by forcing the solution through spinnerets into a current of warm air which removes the solvent by evaporation.

Cellulose acetate plastics first became available in this country in 1927. The acetone soluble cellulose acetate is combined with plasticizers such as

dimethyl phthalate, dibutyl tartrate and triphenyl phosphate. It is mixed in kneaders in the presence of acetone and alcohol and is then worked on roll mills where pigments and dyes are incorporated. For molding powders the solvents are evaporated and the material is ground to the desired size of granules. For cut sheets, slabs from the roll mill are stacked and pressed under heat into solid blocks about 24 x 54 x 6 inches. The blocks are sliced on a planer into sheets 0.005 to over 1.0 inch thick. The sheets are seasoned to remove volatile solvents and are heat-polished by pressing between polished nickel-plated steel plates. For films and foils, a solution ("dope") is cast on a moving polished surface. The volatile solvents are evaporated and the resulting film is stripped, dried and wound into rolls. Films 0.0005–0.01 inches thick can be made by this process.

Cellulose acetate plastics are thermoplastic. They are softened by the application of heat and harden again upon cooling. This cycle of softening and hardening may be repeated indefinitely without any chemical change taking place in the material.[30]

Esters of Other Organic Acids

Esters of most of the common members of the fatty acids have been prepared. In general the methods used for preparing the acetate are applicable to the other members. Cellulose formate may

be prepared by reacting cellulose with anhydrous formic acid in the presence of a catalyst, such as gaseous HCl or $ZnCl_2$. The propionate may be prepared by reacting cellulose hydrate with propionic anhydride in the presence of acetic acid as a catalyst. The butyrate may be prepared by the use of butyric acid, butyric anhydride and $ZnCl_2$ as the catalyst. The higher fatty esters, such as the palmitate, laurate, stearate, linolenate, oleate, and linoleate are prepared by reacting cellulose with the corresponding acid chloride in the presence of pyridine and benzene. It is interesting to note that the cellulose ester of the unsaturated linolenic acid is an oil, soluble in hydrocarbons and turpentine. The esters of linoleic and oleic acids become insoluble by oxidation in air or by heating. Mixed esters of any of the acids may also be prepared, either by using esterification mixtures or by partial esterification with one acid followed by another.

Of all the cellulose esters of organic acids that may be prepared, cellulose acetate remains the only one of technical importance for rayon. Aside from higher costs of production and manufacturing difficulties with most of the other esters, it is found that with increasing size of the acid radical from acetate to stearate and naphthenate, the tensile strength decreases from 10 kilograms per square millimeter for the acetate to 0.3 kilograms per square millimeter for the naphthenate. The elongation increases from 15–25% for the acetate to 110% for the naphthen-

ate. The mixed esters show similar behavior, their properties being intermediate between those of the two acids.[9]

In the plastics field, on the other hand, a mixed ester is finding wide commercial applications. This is cellulose acetate butyrate. It is made by using a mixture of butyric and acetic acids and their anhydrides. The mixed ester has a greater solubility in a wide range of solvents and is compatible with a greater number of plasticizers than the straight acetate. Plasticized mixed ester compositions have a greater resistance to water and alkali and better weathering resistance. Lacquers made from these compositions have greater adhesion than if made from the acetate. Although the mixed esters are higher in cost than the acetate, this is partly offset by their solubility in common solvents and their ability to produce finishes of superior characteristics for particular uses.[30]

Cellulose Ethers

The cellulose esters are easily hydrolyzed. This is a disadvantage for some technical purposes. The cellulose ethers are more attractive in this respect, being stable towards acids and alkalies.

Methyl cellulose is prepared by the action of methyl sulphate or chloride on alkali cellulose. There are three types of methyl ethers depending on the

degree of substitution: (1) The ethers with the highest degree of substitution, approaching a methoxyl (CH_3O) content of 45.6% corresponding to the trimethyl derivative, are soluble in organic solvents, have plastic properties, and good resistance towards water. (2) The ethers with 22–26% methoxyl are soluble in cold water. In these products about 1.5 hydroxyl groups per $C_6H_{10}O_5$ unit are methylated. (3) The ethers with about 5% methoxyl are soluble only in dilute alkali solution. The other alkyl ethers may be prepared in the same way, namely by the action of the corresponding alkyl chloride on soda cellulose or in the presence of an organic base such as pyridine.

The solubility of ethyl cellulose also varies with the degree of substitution. An ether with 5% ethoxyl (C_2H_5O) is soluble in sodium hydroxide solutions on freezing. An ether with about 27% ethoxyl, corresponding to the mono-ethyl derivative is soluble in water, ethyl alcohol, and acetic acid. The usual commercial product is the derivative with 47–48% ethoxyl which has been substituted to the extent of 2.4–2.5 ethoxyl groups per anhydroglucose residue. It is soluble in a wide range of organic solvents including drying oils. The specific gravity of ethyl cellulose is 1.14. This compares with 1.37 for cellulose acetate and 1.65 for cellulose nitrate.

Benzyl cellulose, in the form of the dibenzyl derivative is very resistant to water, is not attacked

by acid and resists alkali attack up to 20% sodium hydroxide solution.[24]

Ethyl cellulose plastics are finding increased uses in industrial applications. Plasticized ethyl cellulose is applied as an insulation for wire by a process of extrusion. This coating will not crack and will resist the tendency of the wire to cut through the insulation under high temperature usage. Ethyl cellulose plastics are also used for the extrusion of strips for the manufacture of modern furniture to take the place of reeds or canes normally employed. The finished furniture is very attractive because of the wide possibilities for bright colorings. Another use for ethyl cellulose in sheet form is for the fabrication of transparent rigid containers. The material, in gages of 0.003–0.020 inches, possesses a number of unique properties, such as flexibility, toughness, dimensional stability, low moisture absorption, ease of fabrication and of printing which readily adapt it to the production of such containers. There is also an increasing use of ethyl cellulose plastics for injection molding of a wide variety of articles having the outstanding properties of toughness, unusual water resistance and excellent dimensional stability.[30]

MODIFIED CELLULOSE

Modified cellulose refers to the early products of degradation of cellulose as a result of swelling with alkaline solution, regeneration of its derivatives, hydrolysis and oxidation. Only those cellulose products which still retain their fibrous structure are now considered in this category. In this state it is very important to be able to evaluate these fibrous partially degraded celluloses, since their appearance in technological applications, such as in the textile and paper industry is of great significance. When degradation has proceeded to the stage where the fibers begin to disintegrate to a powder, a complex mixture of water soluble decomposition products are obtained which are extremely difficult to characterize and which have no technological importance.

Cellulose Hydrate

A number of cellulose products, such as mercerized cellulose and the so-called regenerated celluloses such as viscose rayon, cuprammonium rayon and deacetylated cellulose acetate, differ markedly in physical properties from native cellulose. These

58

properties include their capacity to swell and absorb water, their enhanced chemical reactivity, their increased affinity for dyes, and their solubility in dilute alkalies. These products, however, were found to have a low reducing value, similar to that of native cellulose, thus indicating that the glucosidic linkages of the cellulose chains had not been ruptured.

It was at first believed that these modified celluloses had acquired water of hydration and hence were termed cellulose hydrate. This term has been retained even though it was found later that on careful drying the water could be driven off without changing the properties of the cellulose. The term regenerated cellulose is now synonymous with cellulose hydrate.

An X-ray diffraction pattern of the product furnishes the best means of identifying cellulose hydrate. Such patterns have shown that the hydrate differs from native cellulose in having an expanded crystal lattice, thus offering the explanation for its altered properties. The increase of absorption of moisture at constant relative humidity is roughly in the ratio of 1:1.9 for cotton and rayon showing its increased absorbing surface or capacity.

Hydrocellulose

The treatment of cellulose with dilute acids results in a marked change in the physical properties

of the fibers, such as strength and tenacity. This effect was recognized early in the textile industry. Girard was the first chemist to investigate this effect in detail in 1875. He termed the product hydrocellulose because of the erroneous conclusion that it contained an added water of hydration for each $C_{12}H_{20}O_{10}$ group.

Native cotton has a slight reducing action in alkaline solutions containing cupric salts. This reducing power, when determined under carefully standardized empirical conditions, has been termed the "copper number." It means the number of grams of metallic copper reduced from Cu^{++} to Cu^{+} by 100 grams of cellulose product. In a carefully purified cotton, the copper number is never zero, but may be as low as 0.02 grams. This low reducing value is accounted for by the fact that in the molecular chain of anhydroglucose units, the unit on one end is free to resume its tautomeric form and react as an aldehyde, i.e:
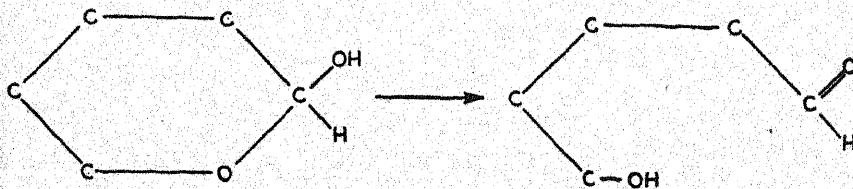
This minimum copper number would presumably correspond to a single terminal reducing group in a giant molecule of some 3,000 anhydroglucose units. In the simple sugar, glucose, which is formed by

complete hydrolysis of cellulose, the copper number is about 300. Somewhere between these two values lies the region of the hydrocelluloses.

In distinction to cellulose hydrate, hydrocellulose is cellulose which has had some of the glucosidic linkages of its chain molecules ruptured. The shortened molecular chains are also shown by the lower viscosity (in cuprammonium solution) of hydrocellulose relative to the higher copper number. A given viscosity corresponds to the same copper number irrespective of the acid treatment. Both accurately indicate the strength of cotton textiles, strength varying directly with viscosity and inversely with copper number.

The solubility of hydrocellulose in cold sodium hydroxide solution increases with increasing copper numbers.

Oxycellulose

The damaging effect of oxidation on cellulose was first observed in technical applications, particularly during the bleaching of textiles. Witz, in 1882, was the first to investigate this action and to adopt the term oxycellulose for the modified product.

There are two extreme types of oxycellulose: (1) The methylene blue type is produced by alkaline oxidation such as by treatment with alkaline hypobromite. It has a low copper number, a marked

affinity for basic dyes such as methylene blue and an abnormal retentive power for alkali. (2) The reducing type is produced by acid oxidation such as by treatment with chlorine water. It has a relatively high copper number, does not readily adsorb methylene blue and shows excessive loss in weight and tensile strength when boiled with dilute alkali.[24]

The presence of oxycellulose in textiles or paper causes reduction in strength and therefore is objectionable. Care must be exercized in bleaching in order to avoid overbleaching and formation of oxycellulose. Besides the formation of carbonyl and carboxyl groups, the average cellulose chain length is also shortened.

CHAPTER VIII

CONSTITUTION OF CELLULOSE

IT HAS been known for a long time that cellulose could be hydrolyzed nearly quantitatively to the monosaccharide d-glucose. It was, therefore, recognized early that cellulose was built up by a process of polymerization of many glucose units into a large molecule. It was seen that, before the structure of cellulose could be elucidated, the configuration of its building unit, d-glucose, had to be solved first. This was finally achieved by Haworth in 1926[12] and progress in the structural study of cellulose was thereby greatly accelerated.

Before Haworth, glucose and the analogous saccharides were formulated as penta hydroxy aldehydes or ketones. Discovery of two crystalline α- and β- forms of methyl glucosides derived from the same d-glucose, required a representation of these compounds as cyclic structures. These were formulated by Emil Fischer as five-atom rings on theoretical considerations without experimental sanction:

$$
\begin{array}{ccc}
\text{CHO} & \text{HCOCH}_3 & \text{CH}_3\text{OCH} \\
\text{HCOH} & \text{HCOH} & \text{HCOH} \\
\text{HOCH} & \text{HOCH} & \text{HOCH} \\
\text{HCOH} & \text{HC} & \text{HC} \\
\text{HCOH} & \text{HCOH} & \text{HCOH} \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH} & \text{CH}_2\text{OH}
\end{array}
$$

|GLUCOSE | α—METHYL GLUCOSIDE | β—METHYL GLUCOSIDE |
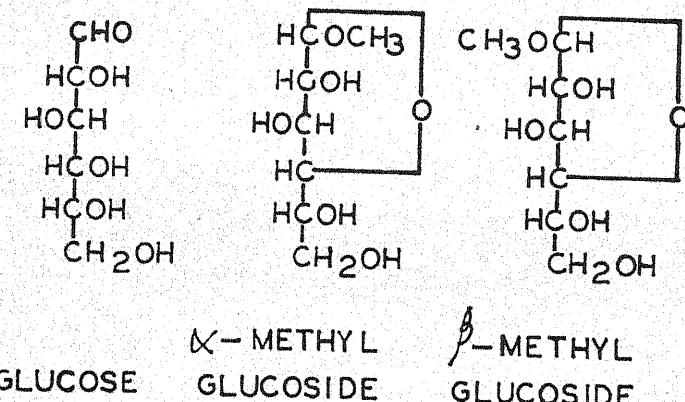
The bearing of the glucoside structure upon the problem of cellulose constitution lies in the fact that the attachment of any alcohol group at the reducing position of glucose is analogous to the attachment of another glucose residue in disaccharides and then another to form the trisaccharide and so on through the higher members of this series until the long-chain polysaccharide cellulose is formed.

Corresponding to the existence of two well-characterized crystalline α- and β-methyl glucosides, there also exist two well-defined crystalline forms of α- and β-glucose with widely different optical rotary values. By mutarotation in solution the one form changes into the other until dynamic equilibrium is attained. It is to the existence of these two modifications of *d*-glucose and their glucosides that the occurrence of polysaccharides of such widely divergent properties as cellulose and starch

is to be attributed, although both of these polysaccharides yield the identical *d*-glucose on complete hydrolysis.

Haworth and coworkers [14] [15] were able to establish the fact that glucose and all the normal sugars should be represented by a six-atom ring structure consisting of five carbon atoms and one oxygen atom and related to the structure of pyran:
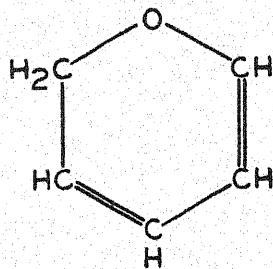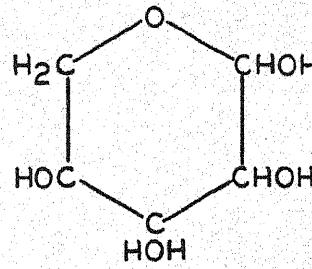
PYRAN   PENTOSE

Differences in configuration in the pentose, represented by distribution of the hydroxyl groups above and below the plane of the ring molecule, account for the existence of four *d*-pentoses, i.e., xylose, arabinose, lyxose and ribose, each existing in an alpha (α) and beta (β) form:

XYLOSE ARABINOSE
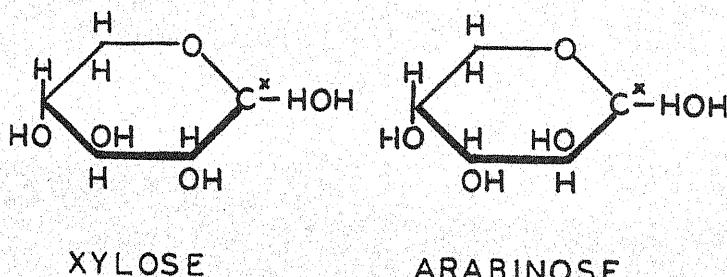
C* indicates the reducing group which may assume its tautomeric form and react as an aldehyde. The structural formulas are represented with heavy shading on the lower side in order that they may be visualized better as they would appear in space, with their various groups above or below the plane of the ring. The problems involved in cellulose chemistry are mainly stereochemical in common with the general chemistry of the carbohydrates, and the use of atomic models is of advantage in understanding them.

In the hexose series, to which glucose belongs, there is an additional carbon atom (number 6) in a side chain carrying a primary alcohol group. The hydroxyl group on the potential reducing group may be placed below or above the plane of the atoms constituting the ring, forming thereby α- or β-glucose, which differ only in this stereochemical arrangement:

α-GLUCOSE   β-GLUCOSE
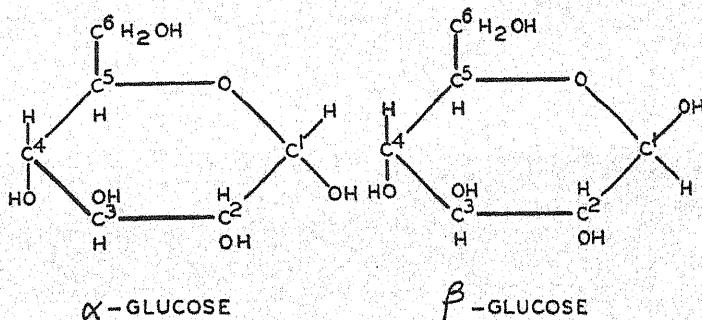
β-glucose represents the most symmetrical arrangement of hydroxyl groups, alternately above and below the plane of the central atoms in the ring. It is this symmetrical arrangement of groups in space which results in the perfect symmetry of the cellulose molecule.

By controlled hydrolysis, starch yields maltose and cellulose yields cellobiose. These disaccharides are identical in composition but not in stereochemical configuration:

α-GLUCOSE   α-GLUCOSE   β-GLUCOSE   β-GLUCOSE

MALTOSE   CELLOBIOSE
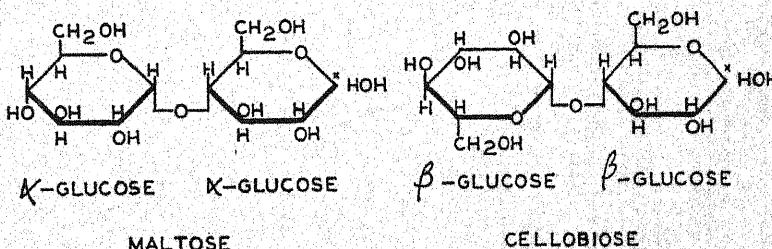
Maltose is composed of alpha-glucose and cellobiose of beta-glucose, each monosaccharide linked

to a second glucose unit through their 1:4 carbon atoms. No other disaccharide than cellobiose has ever been obtained from cellulose. For the polysaccharide, therefore, long chains of this biose anhydride are linked together to form the cellulose molecule:
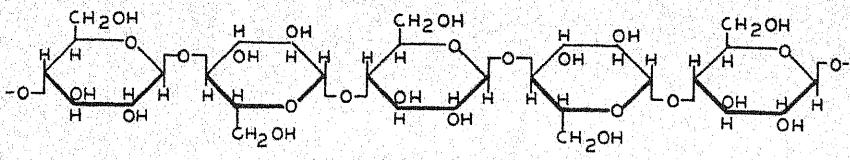
CELLULOSE

Starch has the following structure:
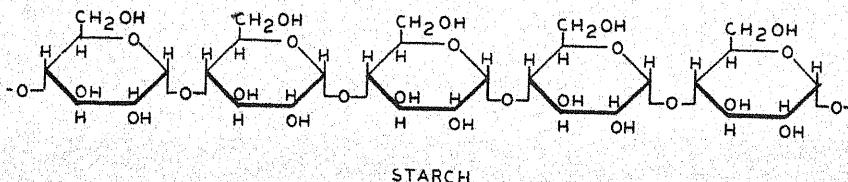
STARCH

The symmetry of this kind of structure is due to the continuous linking of the hexagons at the 1:4 positions, analogous in the benzene series to the para-positions. The cellulose model has the more perfect symmetry in that the side chains carrying the primary alcohol group of the glucose residue are alternately above and below the chain molecule. The cellulose molecule has an overall straight line structure, but the units are actually in zig-zag arrangement by the circumstance that each alternate

anhydroglucose unit is rotated through 180°. This factor is largely responsible for the occurrence of cellulose as a fiber. Starch on the other hand has a curving irregular spiral molecule.

Caesar and Cushing [5] have shown that, by mechanical construction of molecular models using the Fisher-Hirschfelder atomic models, the cellulose molecule yields an essentially straight chain or linear configuration, while the starch molecule yields a helical spring configuration.

If the hypothesis of the molecular chain of cellulose is correct it follows that each of the terminal glucose residues should have one more hydroxyl group open to methylation than the other glucose residues composing the chain. On subsequent hydrolysis of the methylated cellulose, a certain proportion of the resultant fission products should be tetramethyl glucose while the rest are trimethyl glucose. This has actually been done by Haworth, giving rise to the end-group method for the determination of chain length.[13]
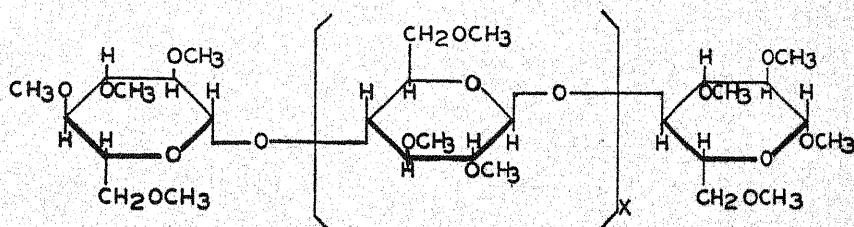
The glucose residue on the left yields tetramethyl glucose on hydrolysis. The others yield 2, 3, 6-tri-

methyl glucose and methyl alcohol split off from the methylated glucosidic group on the right.

The values obtained by this method were 100–200 anhydroglucose units in the cellulose chain. This work proved to be important in confirming the structure of cellulose. However, it is now known that the cellulose chain is actually very much longer. The end-group method does give a measure of the chain length of the end product. However, in order to introduce the theoretical percentage of methoxyl groups to make certain that the cellulose is fully methylated, it is necessary to start with cellulose which has been fully acetylated. Such acetylated cellulose were shown by Kraemer [20] to have a degree of polymerization of 175–360 as compared to about 3,500 for native cellulose, i.e. degradation occurred during acetylation.[39]

Molecular Weight of Cellulose

The classical methods of determining molecular weights, such as elevation of boiling point and lowering of freezing point, have been of little value in studying cellulose. All physical evidence have served to indicate that cellulose was a long-chain polymeric material of high molecular weight which retained its colloidal dimensions in dispersion. The length of the chain may vary within wide limits. Usually, therefore, when speaking of the chain length or molecular weight, an average value is

meant. It has been found useful to refer to this value as the "degree of polymerization" or D.P. meaning the number of anhydroglucose residues per molecule.

The degree of polymerization of various cellulose products as found by Kraemer [20] are given in Table No. 1. They are based on determination, by means of the Svedberg ultra-centrifuge, of cellulose dispersions in cuprammonium solution and the cellulose derivatives in acetone solution.

TABLE 1

Substance	*D.P.*	*Molecular Weight*
Native cotton cellulose	>3,500	>570,000
Purified cotton linters	1,000–3,000	150,000–500,000
Wood pulps	600–1,000	100,000–160,000
Commercial regenerated cellulose .	200– 600	30,000–100,000
Beta-cellulose	15– 90	2,400– 14,500
Gamma-cellulose	<15	<2,400
Dynamite nitrocellulose	3,000–3,500	750,000–875,000
Plastics nitrocellulose	500– 600	125,000–150,000
½ sec. lacquer nitrocellulose	175	45,000
Commercial secondary cellulose acetates	175– 360	45,000–100,000

A molecule of native cellulose of a degree of polymerization of 3,500 corresponds to an actual length of about 1.8 microns, or a ratio of length to diameter of over two thousand. If they were not so thin, a molecule of this length would be easily visible under the microscope.

Kraemer has obtained definite evidence to indicate that the units in solution are truly molecules in the chemist's sense of the term and are not colloidal aggregates. The molecule itself is so large that it is a colloidal particle.

MICELLAR STRUCTURE OF CELLULOSE

A COMPREHENSIVE discussion of the crystalline and micellar structure of cellulose would require a book in itself. Modern conceptions of the fine structure of cellulose are excellently portrayed by Mark, and this chapter is based largely on his published work.[22, 23]

In 1858, the botanist Naegeli proposed the "micellar theory" of the organized structure of natural materials based on his studies of double refraction, swelling, and mechanical properties. Naegeli concluded that such materials as starch granules, cellulose fibers, and proteins are not built up directly from their molecules but rather from submicroscopic *groups of molecules* which he called micelles (this term being derived from the Latin *mica*, meaning a crumb or something that breaks off). On the basis of the anisotropic optical and mechanical properties, i.e., physical properties which are more pronounced in one direction than another, such as double refraction, Naegeli concluded that each micelle acted as a small crystal or crystallite and that these properties were due to regular orientation of the micelles. Naegeli's theory of the submicroscopic crystallites received little attention

at that time, but in its extended form, it is now-recognized as the fundamental basis upon which most of the present conceptions of the structural chemistry of fibrous materials are built.

The shape of the molecule cannot be "seen" by the human eye even with the aid of the most powerful microscope, because the rays of visible light are a thousand times too coarse for the task. The rays which are most suited for the purpose of examining the shapes and arrangement of atoms and molecules are the X-rays, because their wave-length is some 10,000 times shorter than ordinary light. The micron which is 1/10,000th of a centimeter in the optical microscope is equivalent to the Angstrom unit (Å) (which is 1/10,000th of a micron), by X-ray technique. The wave-length of X-rays is of the same order of magnitude as the distance between contiguous atoms in crystals, i.e., 1 Å or 10^{-8} centimeters.[3]

The first X-ray evidence of the crystal structure of cellulose was obtained as early as 1913. Progress in this field became rapid after the organic chemists had established the chemical nature of the main-valence chains of cellulose. It was then shown that cellulose from all sources consisted of definitely arranged crystallites. The study of X-ray diffraction patterns led to the establishment of a unit cell with the following dimensions:

a—8.35 Å, b—10.3 Å, c—7.9 Å and β–84°, the b axis being in the fiber direction (Fig. 9).

Each unit cell is monoclinic in structure and con-

tains the equivalent of four anhydroglucose resi-
dues. These residues in the form of chains of hex-
agonal rings are arranged parallel to the *b* axis of
the unit cell, with one cellobiose group on each
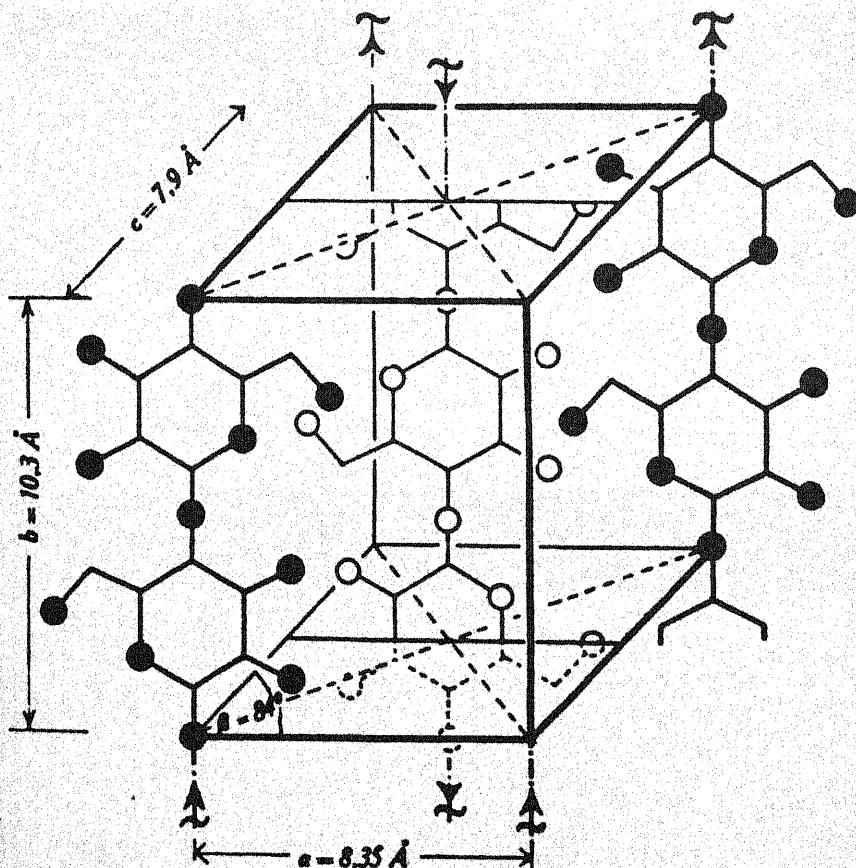
FIG. 9. Schematic model of the crystalline unit cell of cellulose (From Meyer and
Misch, *Helvetica Chimica Acta*).

corner and one through the center. They form the long main valence chains arranged in the direction of the fiber axis and held together laterally by
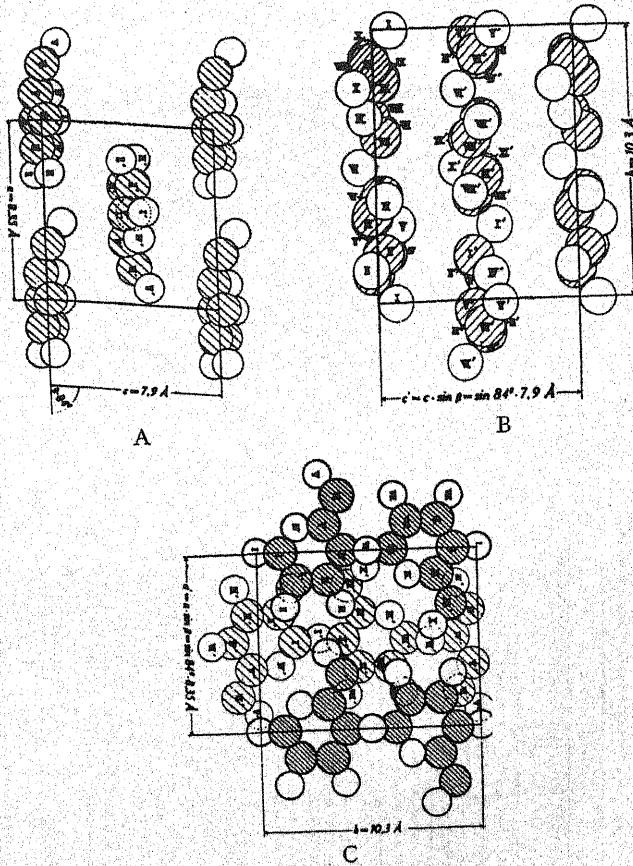
FIG. 10. Atomic model of cellulose proposed by Meyer and Misch based on actual dimensions. A. *ac* plane perpendicular to *b* axis. B. *bc* plane perpendicular to *a* axis. C. *ab* plane perpendicular to *c* axis. The clear circles represent oxygen atoms and the shaded circles carbon atoms.

secondary valence forces. The anhydroglucose units in the main valence chains are arranged alternately in such a way that a half turn occurs for each unit in height. Adjacent chains in the *a-b* plane are arranged so that the primary hydroxyl groups in one anhydroglucose unit is next to the secondary hydroxyl groups in the anhydroglucose unit of the neighboring chain.

Another view of these relationships is presented in the model proposed by Meyer and Misch [23, 26] based on actual atomic and molecular dimensions (Fig. 10) and in the spatial model prepared by the author showing the schematic relationship of the three planes in the unit cell (Fig. 11).

In the direction of the *b* axis the main valence chains are kept together by glucosidic bonds between carbon atoms 1 and 4 of two adjacent anhydroglucose units. The strength of these bonds is of the order of 50,000 calories per mol in terms of the energy required for their dissociation.

Along the *a* axis the centers of the two nearest oxygen atoms of two anhydroglucose residues approach each other to about 2.5 Å. If these were only Van der Waals' forces acting between them they should not approach closer than 3.0 Å. This means that stronger forces are acting between the two oxygen atoms in the crystal lattice and it is assumed that a hydrogen bond is established between them. This would correspond to a strength of about 15,000 calories per mol. This would ex-

plain the relatively tight packing in the a-b plane in the direction of the a axis and also offer an explanation for the fact that more highly oriented
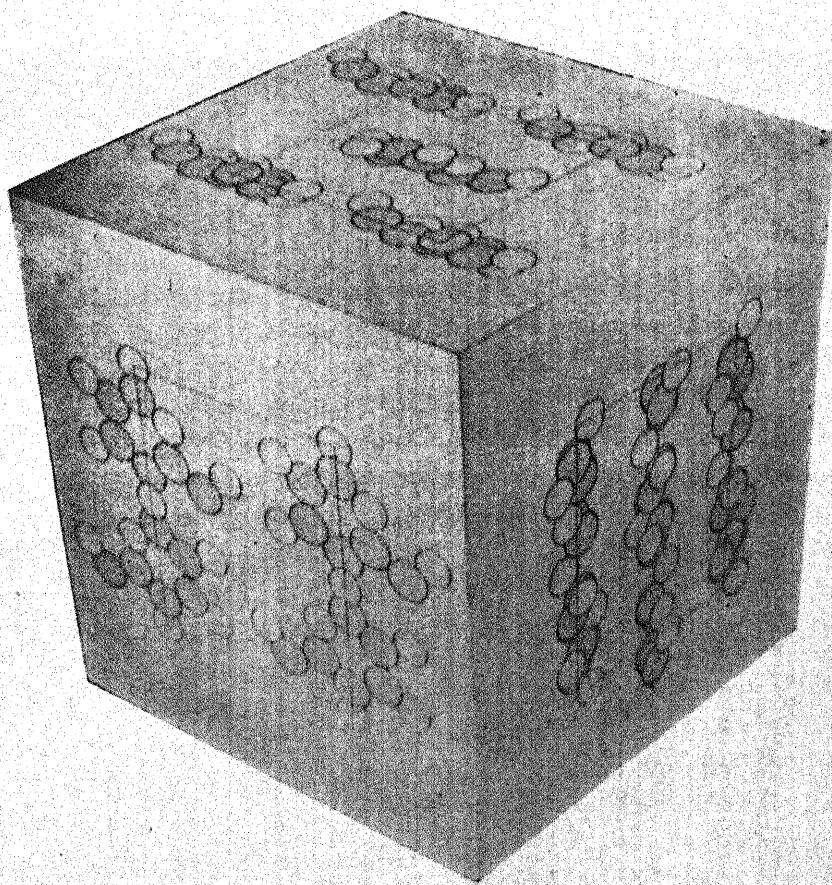
FIG. 11. Spatial model, showing the schematic relationship of the three planes of Fig. 10.

crystallite structures can be obtained by mechanical treatment, such as stretching in the swollen state.

Along the *c* direction, the nearest distance between atomic centers is 3.1 Å between carbon and oxygen, or 3.8 Å between the hydroxyl groups of two chains. This corresponds closely to the distance to be expected if Van der Waals' forces hold the lattice together in this direction. Such forces correspond to a strength of about 8,000 calories per mol.

The crystal lattice of cellulose then may be regarded as a combination of a chain lattice and a layer lattice. The strongest forces act along the *b* axis. These are the main-valence glucosidic bonds in the fiber direction. The forces along the *a* axis are also comparatively large with hydrogen bond nets in the *a-b* plane. Perpendicular to this plane, however, weaker forces are active and the spacing between these planes is relatively large. This permits chemical reagents to penetrate more easily into the crystallite lattice and to react with the hydroxyl groups of cellulose.

Confirmation of the picture just presented is given by the expanded crystal lattice of mercerized and hydrate cellulose as determined from a study of the X-ray diffraction patterns:

	Native Cellulose	*Mercerized Cellulose*	*Ammonia Cellulose*
a axis	8.35 Å	8.1 Å	9.83 Å
b axis	10.3 Å	10.3 Å	10.3 Å
c axis	7.9 Å	9.1 Å	10.05 Å
β	84°	62°	53.5°

The distention of the crystal lattice in the *c* direction allows room for the penetration of foreign molecules and accounts for the greater swelling and enhanced chemical reactivity of mercerized cellulose.

Normally only Van der Waals' forces are weakened by alkali treatment, moving apart the *a-b* planes but leaving the stronger forces in the *a*-direction intact. However, Barry, Peterson and King obtained an ammonia cellulose by treating ramie fiber in liquid ammonia, which gave the above crystal lattice. This is still more distended than the mercerized lattice and shows a weakening of secondary valency forces in both the *a-* and *c-* directions. These investigators also showed that the ammonia treatment was a reversible reaction. When the ammonia cellulose was decomposed with water, they obtained the same X-ray pattern as for untreated ramie. It had previously been regarded that alkaline swelling and hydrate formation was an irreversible reaction.[24]

X-ray measurements have also led to an indication of the size of the micelle in which these crystal lattices occur. These were found to have an average width of about 50 Å and a length which is longer than about 600 Å. The exact dimensions are in doubt and there is controversy over the assumptions which must be made in obtaining these measurements.

However, by means of X-rays it was shown that what Naegeli had proposed on purely theoretical grounds nearly three quarters of a century before

was correct, namely, the existence of micelles, their crystalline character and allignment in the fiber direction.

There still remained the much debated question as to what held these micelles together, or in other words, what the inter-micellar substance in the fiber was. The answer was first suggested in 1930 [8] as the result of a study of the structure of gelatine, namely, the continuous micellar theory as opposed to Naegeli's "disperse" micellar theory. This theory has been ever more widely developed and accepted and now presents a most satisfactory and logical picture of the ultimate structure of cellulose fibers.

The "disperse" micellar theory involves the conception of the existence of discrete brick-like, crystalline particles which are orientated with respect to the fiber axis and are separated by amorphous material. The micelles were considered to retain their orientation during intermicellar swelling and to be dispersed in their original dimensions during the early stages of dissolution.

When it was first brought out by Staudinger [36] from viscosity studies that the cellulose chain molecule was some ten times longer than the estimated size of the micelle, it became necessary to revise the earlier views and this eventually led to the conception of the continuous micellar theory. If it is assumed that the crystallization regularity of the cellulose chain lattice is interrupted by regions where the chains are not sufficiently close or regular

to form a crystal lattice, then these regions would produce in the X-ray diagram the same effect as though they were amorphous material separating well-defined crystallites. Those regions in the cellulose fiber which possess a definite crystalline regularity of cellulose chains are the "crystallites" or micelles. The other regions in the fiber structure where the chains have an irregular arrangement, are the "amorphous" or "inter-crystalline" cellulose.

It has now become possible to extend the applicability of the X-ray method to the study of non-crystalline or amorphous portions of cellulose. It was thus shown that the amorphous portions of the cellulose could be altered. Extreme swelling of native cellulose with quaternary ammonium bases gave an X-ray diagram of diffuse rings, just as for a completely amorphous material. After stretching the swollen cellulose, a fiber diagram was again obtained. It is thus entirely analogous to rubber which gives an amorphous diagram when relaxed and a fiber diagram when stretched. Other similar experiments gave the same results. A normally produced viscose filament was found to contain about 40% crystallized and 60% amorphous cellulose. After stretching this filament in the swollen state about 70% became crystallized.

It was found that the chains in the non-crystalline portions do not lie entirely unordered but form bundles *approximately* parallel to the fiber axis. These do not give rise to sharp interference spots

on the diffraction pattern because the chains are not oriented enough. The crystalline regions may be compared to a bundle of well-shaped pencils forming a regular structure; the non-crystalline portions may be compared to a bundle of irregular sticks all lying in a certain direction, but forming a structure full of irregular intermediate spaces. The increase of crystallized portions which is created during the stretching is due to the fact that the 'secondary forces between the chains are allowed to react by bringing the different atoms in positions of their minimum potential energy. Stretching in the dry or insufficiently swollen state produces the reverse effect, causing a weakening of the structure.

From the work required to break the ultimate atomic bonds, Mark [22] made some theoretical calculations of the fiber strength that would be expected if a fiber were made up of one continuous primary valence chain. A calculated tensile strength of 800 kilograms per square millimeter was thus obtained. It was interesting to find by actual measurements of the strength of various fibers that several specimens gave values corresponding very closely to the figure for an ideal sample of infinite chain length. Even ordinary flax fiber has a tensile strength of over 100 kilograms per square millimeter, while well-oriented viscose is not much less with 80 kilograms per square millimeter. These values compare with that of the best steel which has a tensile

strength of about 170 kilograms per square milli-
meter.

This high strength of cellulose fibers is not easy
to understand. Every chain in the actual sample
must have an end somewhere and this point should
be a potentially weak spot.

Mark [22] presents the following working hypothe-
sis to explain this behavior (Fig. 12). "Consider
the two molecular ends A and A'. It is apparent that
if they were not inside a crystallized region in the
material under the influence of a stress, they might
be separated from each other quite easily, since they
are held together only by the weak intermolecular
forces. But since the ends lie in a crystallized region
of one micelle they are kept in their positions not
only by the forces between A and A', but also by
the Van der Waals' forces along the two lengths
AB and A'B'. In order to separate the two mole-
cules it is necessary to pull them out of the lattice
and to overcome all the forces along the length with
which they are held inside of the crystallized region.
If the parts of the main-valence chains which belong
to the micelle are long enough, then the total energy
required to pull them out of this range will be great
because the two ends of the chains are entirely con-
cealed in the center of the micelle and on this ac-
count do not form a potentially weak spot for the
rupture of the filament. The line of chains which
is designated by small crosses behaves like a single
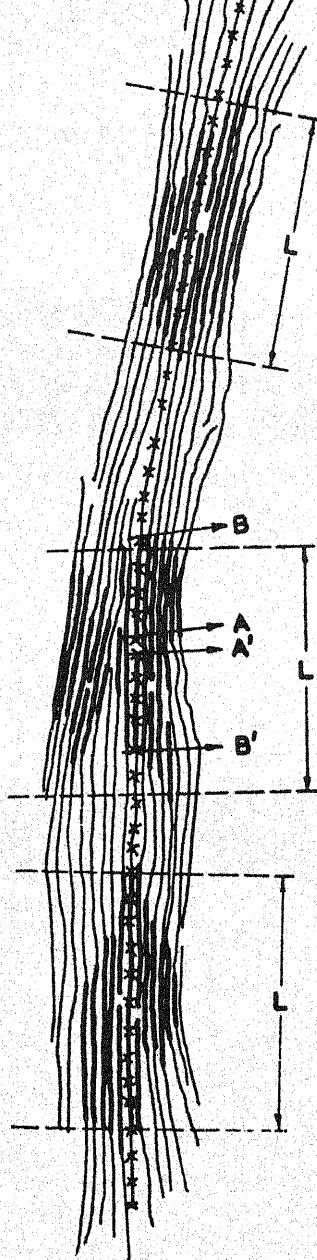
Fig. 12. Diagram showing main-valence chains going through more than one micelle (*From J. Physical Chemistry*).

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main-valence chain of infinite length. These crystallized regions have the effect of strengthening the fibers by covering up the chain ends inside of the solid structure."

This hypothesis would also explain why there is very little change in mechanical properties when the degree of polymerization of technical regenerated filaments is reduced from about 560 to about 300. However, when a degree of polymerization of less than 200 is reached, the samples show rather poor physical properties, such as tenacity, elasticity and pliability. In the case of native cellulose, there is very little change in strength until the degree of polymerization is reduced to about 700–800, but damage is evident at 600 or less.

The normal valence chains are of considerable length and therefore pass through several micelles tying them together. The chain ends are distributed at random in the micelles and their effect in producing potentially weak spots is rendered negligible by the crystallizing forces. If the length of chains approaches the length of the micelles, it will frequently occur that the end of a chain will coincide with the end of a micelle with the result that the tensile strength of the sample will be determined by the weak secondary valence forces.

The continuous micellar theory reconciles the previous conflicting deductions derived from X-ray and viscosity data. The term micelle is still used. However, it no longer means an individual struc-

tural element but a region where crystalline forces are active and forming part of a continuous organized structure. The existence in solution of long chain molecules, deduced from viscosity data, is made possible because these same chains are present in the original cellulose.

Another difficulty previously encountered was the explanation of the cohesion of swollen cellulose on the basis of non-swelling crystallites. If cellulose is soaked in water, X-ray evidence shows that there is no change in the crystallized regions and that the water penetrates only the amorphous material or clusters of molecular chains built up near the fringes of the micelles. If chain ends occur in these swollen areas, then the tensile strength will be a very sensitive function of swelling. The wet strength of the cellulose fibers depends to a large extent on the average length of the chains. The longer the chains are the larger the amount of crystallized material and the smaller the chance of chain ends occurring in the unordered network of the fringes.

The physical properties of the cellulose fiber, such as tenacity and reactivity, are related to the amount of crystalline material, while the reactivity, such as swelling and ease of chemical reactions, is related to the non-crystalline parts of the cellulose. The mechanical behavior of the fiber is influenced by (1) the relative amounts of crystallized and amorphous fractions, (2) the ratio between the average length of the main-valence molecular

chains and the average length of the micelles or crystallized regions, and (3) the flexibility of the fringes and their sensitivity to swelling and chemical reactions.[22]

The indications are that the small amount of lignin that occurs in the secondary wall of woody fibers is located in the intercrystalline fringes of the cellulose network. This would account for the greater stiffness and strength of lignified fibers and their much smaller chemical reactivity as compared to pure cellulose. The imbedding of the ideally-amorphous lignin is thus equivalent to an increase in the crystallinity of the cellulose, and is comparable to the toughening that occurs when carbon black is milled into rubber.

The existence of the crystallized regions and intermicellar chain clusters was also demonstrated by an independent method. This involved the introduction of minute crystals of the heavy metals gold and platinum into a filament. The X-ray diagram of the cellulose was not changed, showing that the heavy metal was not able to penetrate the tightly packed inner micellar spaces, but was deposited between the micelles. From their increased scattering power and sharper X-ray diffraction pattern, the heavy metal was found to be distributed in fine lamellar sheets with an average distance of about 50 Å from each other, i.e., exactly the average width of the micelles.

By a modified procedure of depositing the heavy

metal crystals in ramie fiber, it was found possible to determine their average size with the ultramicroscope and, therefore, the average size of the intermicellar holes which they occupy. These large holes were thus found to be of the shape of a lens with a diameter of about 200 Å and a length of about 1,000 Å. Very little is yet known about these large holes, except that they are certainly present and that they play an important part in the behavior of the fiber.

We may look to the electron microscope to fill in this wide gap between the upper range of X-ray technique of about 600 Å and the utmost range of the optical microscope of about 5,000 Å. Ruska and Kretschmer [32] thus report the observation by means of the electron microscope of threads 50 Å wide and several microns long, corresponding to the width of a micelle but considerably longer. They found other fibrillar fragments from the degradation of cellulose fibers which were 100–1,000 Å wide and 0.5–2 microns long.

To summarize briefly our present knowledge about the structure of a cellulosic fiber, we may conclude with the following figure proposed by Mark (Fig. 13).

This figure is drawn with the assumption that we would have a microscope the amplification of which could be changed step by step, always increasing by a factor of 10 to the point where 1 Å would be 1 centimeter.
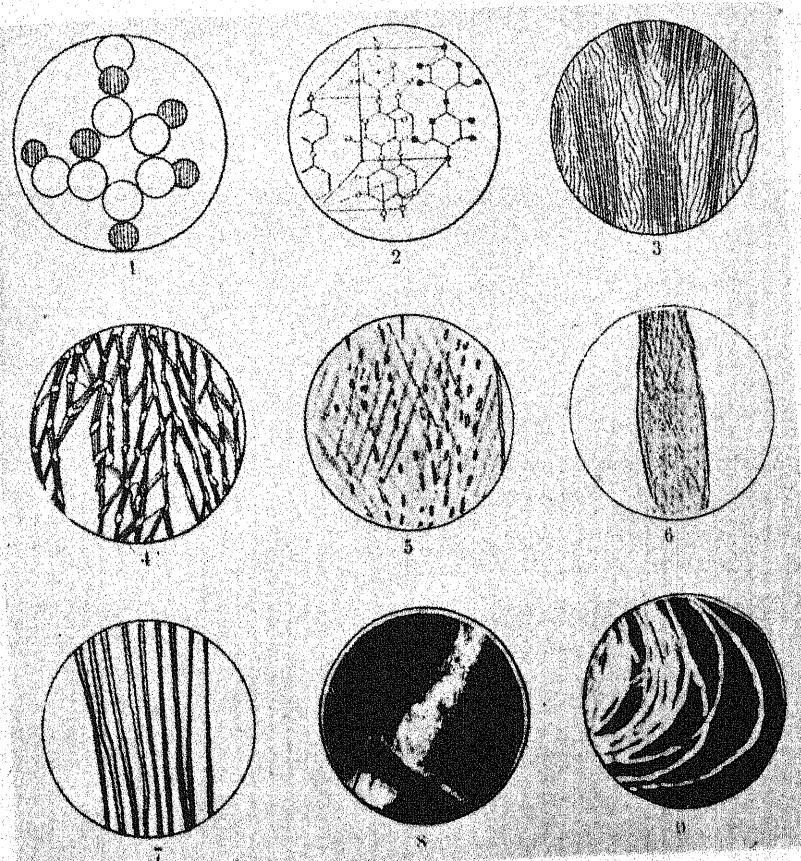
FIG. 13. Complete structure of a cellulosic fiber as summarized by Mark. 1. Glucose unit. 2. Unit cell. 3. Micelles and amorphous areas. 4. Network of crystallized and amorphous regions. 5. Fibrillar structure. 6. Single fiber. 7. Group of fibers. 8. Single yarn. 9. Skein of rayon yarn. (From J. Physical Chemistry.)

In picture 1 of this figure we see the fiber at the highest amplification of 1 to 100,000,000, showing the atoms and the anhydroglucose units as the ultimate chemical element of cellulose. Switching to the next amplification of 1 to 10,000,000, the elementary unit cell of the cellulose crystal is revealed. The next picture at an amplification of 1 to 1,000,-000 shows the crystallized portions of the fiber, the micelles and between them the amorphous parts. In the fourth picture at an amplification of 1 to 100,000 we see a representation of the network of crystallized portions (parallel lines) combined and linked together by the flexible amorphous regions and the large irregular holes between them. The fifth picture with an amplification of 1 to 10,000 is near the utmost range of the optical microscope and shows the fibrils. The sixth picture at an amplification of 1 to 1,000 is well within the limits of microscopical observation and shows a single cotton fiber. The seventh picture at an amplification of 1 to 100 shows a group of fibers. The eighth picture at a magnification of 1 to 10 shows a single yarn. Finally the last picture shows a skein of rayon yarn as seen with the naked eye.

Thus, in nine steps, the range of our present knowledge of cellulose may be seen to traverse a scope extending from the infinitely small to normal vision. We may confidently expect that ever more useful applications of cellulose chemistry will follow our present knowledge of its underlying laws.

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TO

MY WIFE

WITHOUT WHOM THIS BOOK WOULD
NEVER HAVE BEEN WRITTEN